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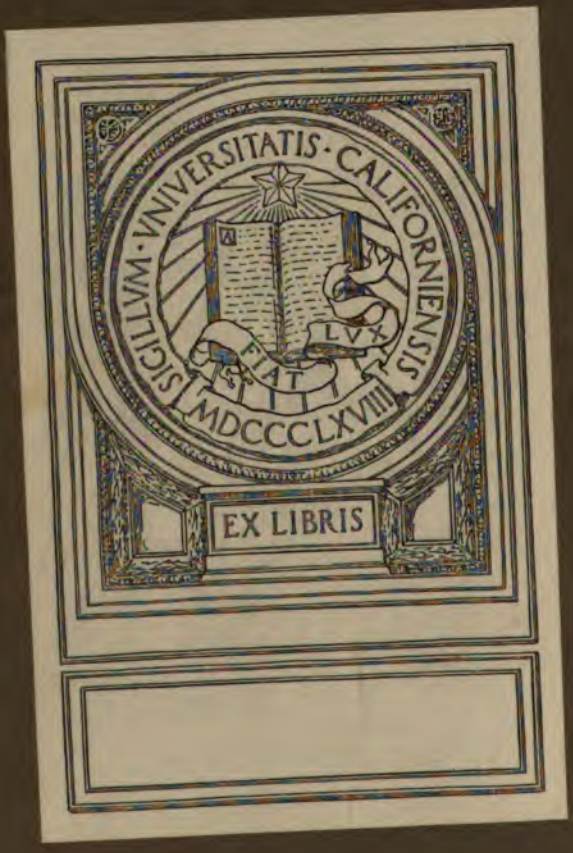
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A TEXT-BOOK

OF

QUANTITATIVE CHEMICAL ANALYSIS.

ILLUSTRATED.

BY FRANK JULIAN.

FIRST EDITION.

THE RAMSEY PUBLISHING CO.
ST. PAUL, MINN.

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"*It is ufual with Chymifts to affert their Principles, Salt, Sulphur, Mercury, and fome add* Caput Mortuum *and Flegm; butwhenwe exactly confider, there is nothing folid to be built upon; for fome call that which is Oyly, fulphur; that which vapoureth, Mercury; that which concreteth, falt; but this doth not fatisfy us of the wifer fort. For we know there is fomething that is not Oyly which is fulphurous, as* Aqua Vitae, *&c. and fometimes vapours, which differs from Mercury, as the Flegma in Stillings. Alfo there are many things that want the oyly part, do they therefore want Sulphur? And the examples they bring to prove it, are more difficult, taken from combuftible wood and anatomy of Vegetables. In the firft example they will have Sulphur reprefented by Butter, Mercury by Whey, Salt by Cheefe. In the fecond they call that fulfur that fumes, Mercury that which fmoaks, falt that which remaineth in the afhes. In the anatomy of Vegetables they fay there is oyl that is Sulphur, Water that is Mercury, and afhes full of falt. But who knows not, but that in Whey there is more falt than in the Cheefe? That foot (which is congealed fume) contains in it self, oyl, falt, and fpiritual water? And fome vegetables have not a drop of Oyl.*"

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CONTENTS.

PART 1.

PAGE

Chapter 1. Introduction 7
2. Sampling. Preparation of the sample for analysis 18
3. The Balance and Weights 29
4. The Operations of Analysis 45
Weighing the Sample 45
Solution 46
Evaporation 57
Distillation 62
Precipitation 68
Separation 74
Filtration 86
Washing precipitates 96
Ignition 100
5. Volumetric Analysis 110
6. Gasometry 139
7. Attributive Methods 155
8. Calculation of Analyses 174
9. Errors and Precautions 190

PART 2.

Reagents 205
Exercises 1. Alcohol 213
2. Lead carbonate — Ferrous sulfate 215
3. Sodium chloride 216
4. Coffee — Ginger 217
5. Cast Iron 219
6. Ether 220
7. Standard acid and alkali 221
8. Vinegar — Lemon juice 223
9. Chloral hydrate 223
10. Acetic acid 225
11. Hydrastis 227
12. Guarana 227
13. Standard permanganate 229
14. Potassium chlorate — Forge scale 229
15. Chrome yellow 231
16. Metol 233
17. Sodium thiosulfate — Steel 234
18. Galena 237
19. Barium chloride 238

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PAGE

Exercises 20. Lard 240
21. Potassium permanganate 242
22. Air — Ammonium sulfate 244
23. Nickel-Copper alloy 247
24. Wollastonite 251
Additional analyses 256

PART 3.

SPECIAL METHODS AND TECHNICAL ANALYSIS.

Colorimetry 259
The Fire Assay 268
Electrolysis 278
The Metals and Common Acids 289
Ultimate Organic Analysis 295
Proximate Organic Analysis 311
Chlorimetry 322
Iron and Steel — Iron Ores 328
Coal 359
Natural Water 366
Fertilizers 382
The Alcohols — Glycerol 398
The Alkaloids 409
The Tannins 421
The Carbohydrates 427
The Oils and Fats 452
Soaps 469
Milk and Butter 476
Urinalysis 493
The Organic Dyestuffs 506

PART 4.

Notes on the Methods of Analysis 521

APPENDIX.

Technical and Industrial Analysis 567
Tables 592
Index 599

PREFACE.

This volume is intended for the aid of students who, having a fair acquaintance with the elements of general chemistry, can devote a limited time to quantitative analysis concurrent with or following the usual qualitative course; and as an introduction to the monographs on special departments of technical analysis for those purposing to engage in some particular branch as a future occupation.

In Part 1, after outlining the general principles of the art, there are described the operations of solution, precipitation, etc., and the appliances commonly employed for the purposes.

Following is a graded series of exercises chosen with a view to illustrate the leading principles in analysis and afford practice in the usual manipulations. They are, for the most part, simple and easy of execution, and call for only such apparatus as is commonly found in the laboratories of educational institutions. Directions are given in full detail and have been closely followed in the analyses whose results are appended.

In Part 3 is considered the analytical behavior of a number of articles of commercial importance. It has been attempted to outline the most approved methods for their analysis and to annotate some others that are of interest from their promise of future development or as suggesting the application of less familiar principles. Working details and criticisms have been largely omitted as they would be useless unless accompanied by particulars and precautions too voluminous for insertion here; for these there may be consulted the standard treatises on the various subjects and the references given, which are, wherever possible, to original articles or abstracts in English.

In Part 4 are presented some notes and observations relating to the principles and practice of the art in general that may be of interest to the student.

To treat with any degree of completeness within the compass of a text-book, a subject so extensive and so essentially one of detail as quantitative analysis is of course out of the question, and in presenting, as is here attempted, a general view of the art as practiced at the present time, there arises the difficulty of deciding as to what matters should be given prominence and what but touched upon. In any event, much of importance can only be referred to and much of interest must be omitted altogether, leaving to the instructor to amplify and particularize to the extent he may consider most profitable to the student.

More prominence than is usual in treatises on quantitative analysis has been accorded to the principles underlying the methods of analysis. This course may not appeal to those who regard analytical chemistry only as a means to a financial end, but a broader view must perceive that the art as a whole will only advance in proportion as the basic principles are better understood, and if it is ever to attain the dignity of a science those who contribute to this end will need a more comprehensive knowledge of the art than is afforded by the study of a string of detailed recipes, however practically useful they may be.

In an appendix I have ventured to discuss at some length certain phases of

the important subject of the practice of technical and industrial chemical analysis. Though much of any comments on a theme of this kind must necessarily be but personal opinions and accepted as such, a somewhat extended experience and observation confirms my belief in the correctness of the views there set forth.

The author will be grateful if his attention is called to any errors that may be noted.

F. J.

CHAPTER 1.

INTRODUCTION.

Quantitative chemical analysis is the art of ascertaining the relative proportions of the constituents of any form of complex matter through the application of physical forces aided by chemical reactions.

It is based mainly on these laws: that the extent of a measurable physical or chemical attribute of a body varies with the mass of the body; especially that at any given locality, weight bears a constant ratio to mass; that among the atoms of every chemical compound there exists a definite invariable proportion; and that every synthesis or decomposition of a molecule or rearrangement of molecules is governed by fixed laws. A successful practice of the art calls for a knowledge of the principles of chemistry, the physical properties of bodies and their chemical behavior, and manual skill to perform the mechanical operations of analysis without loss of the substance analyzed.

Under a strict construction of the term quantitative chemical analysis there are comprehended only those processes involving and depending on chemical reactions, but custom has widened the scope to include also methods based on the measurement of some physical attribute of the substance analyzed and even purely mechanical separations.

Any form of complex matter, animal, vegetable or mineral, may be subjected to a quantitative examination with an outcome more or less successful. For as every art is hedged by current limitations, so an analysis may be easy or difficult or impossible. The common metals, the inorganic acids, a few organic bodies and their compounds have such pronounced and clean-cut relations toward solvents and precipitants that their separation from solutions and from each other can be done with ease and precision, and with a fair degree of skill, exact determinations can be made, or at least sufficiently exact for all practical purposes.

But it is quite the contrary with many mixtures, such as those of the rare earths, the alkaloids, oils, vegetable extracts, etc., which oppose peculiar difficulties against their separation and determination, from their indifference to most reagents and similarity of behavior towards others; and so one is often restricted to reactions ill-defined and modified or obscured by known or unknown influences, and in general must be content with but approximate results even under the most favorable circumstances.

The object for which an analysis is undertaken may be either (A) to ascertain or prove the composition of a chemical compound or derive its empirical or rational formula; or (B) to separate the components of a mechanical mixture, or find the percentage of one or more of the valuable constituents or detrimental impurities in a natural product or an article of commerce. In general, the analysis of a substance belonging to either class follows the same lines, the only difference being in the preliminary treatment of the material, as for the former it is essential that the aggregate of the impurities contained shall at most not exceed the minimum of error inherent to the method adopted for the analysis, and so it is admissible and often imperative that some mode

of purification be resorted to; while with the latter class the only alterations allowable are those of comminution and the removal of hygroscopic water or foreign bodies known to have been accidentally introduced.

The manipulations in solution, filtration, evaporation, etc., are practically the same as those familiarized by qualitative analysis, and only call for greater care to avoid losses and gains during these operations. In addition, there must be learned the arts of weighing, accurate measuring of liquids and gases, and the comparison of shades of colors, besides a certain manual dexterity and lightness in working with fragile glassware and instruments for precise measurements. As in other arts, some will quickly become proficient, others by dint of practice, while a few seem devoid of any sort of mechanical knack.

Terminology.

1. In general, a *gravimetric analysis* is performed by separating successively from a weighed amount of the substance, each of the constituents in the solid form, either isolated or in combination with other elements, and from its weight calculating its proportion in the original substance. Of *volumetric analysis* the basis is a chemical reaction between a constituent and some reagent; the weight of the former being calculated from the weight of the latter required to produce an exactly complete reaction between them, neither remaining in excess. In *gasometry*, from a measured volume of a mixture of gases, each is absorbed in turn by a suitable solid or liquid reagent, the diminution in volume showing its proportion therein. *Attributive methods* are based on the rule that the extent to which a measurable attribute is exhibited by a body is proportional to the mass of the body.

2. In a *proximate analysis* the component species or groups of a chemical compound or a mixture are determined, while an *ultimate analysis* shows the proportions of the elements present. For example, the composition of a mixture of gases may be stated in either of the following ways: —

Proximate Analysis.		Ultimate Analysis.	
Hydrocarbons	71.80	Carbon	68.98
Carbon monoxide	25.60	Hydrogen	14.63
Carbon dioxide	1.50	Oxygen	16.39
Water	.50		

The purpose for which the result is to be employed decides which of the two will be of the greater service; also whether a *partial analysis*, showing but a few of the constituents, will suffice, or a *complete* one giving all (or as many as can be determined) will be necessary.

3. Finding the proportion of any constituent of a compound or mixture is called a *determination*, *estimation*, *trial*, or *test*; if present in the quantity of the substance ordinarily weighed for analysis in so small a proportion as to be unweighable, it is reported as a *trace* or *color*. If only the most valuable or important constituent is determined, the process is termed *assaying* and the result an *assay*;* thus, quinometry, the assay of cinchona bark for quinine; morphiometry, the assay of the poppy for morphine. In metallurgical analysis a *wet assay* is one made by ordinary methods, the reactions taking place in aqueous solutions, while in a *dry assay* or *fire assay* the substance for examination is melted with the proper fluxes in an earthen crucible heated in a furnace.

4. A *method* or *scheme* comprises the directions for performing an analysis, a scheme more usually applying to the complete analysis of a complex ma-

* Chem. News, 1868—1—140, 160, 170.

terial. If carried out exactly as formulated with the exception that the substance to be analyzed is omitted, the determination is called a *blank* or "*dummy*." If there is analyzed along with the sample to be tested and under the same conditions, another sample whose composition is known from a previous analysis by another method, the latter is termed a *parallel determination;* while a *proof* or *synthetic proof* is a mixture made up with chemically pure constituents to the same composition, as near as may be, of the substance to be analyzed, and both proceeded with under uniform conditions.

5. In *volumetric* or *titrimetric* analysis the addition of a measured volume of one solution *A* (the *titrand*) to another *B* (the *titrate*—a solution of the substance to be tested) producing an exactly complete reaction between the two is called a *titration*. The amount of reagent dissolved in a unit volume of *A* or the weight of substance in *B* that this volume of *A* exactly combines with is termed the *titre*, *strength*, or *standard* of *A*, and *A* a *standard* or *set solution*.

Acidimetry is the process of finding the strength of a solution of an acid, usually by the aid of a standard solution of an alkali; *alkalimetry* is the reverse of this. *Chlorimetry* and *iodimetry* are respectively the measurement of free chlorine and iodine by a standard solution of some reducing agent.

6. The decomposition of a solution of a metallic salt by the agency of an electric current is called *electrolysis*, and the salt an *electrolyte*. The conductors through which electricity passes from the solution are termed *electrodes* and are usually platinum plates, the one by which the positive electricity leaves being the *cathode*, and the other the *anode*, the metal from the decomposition of the electrolyte being deposited on the former.

The methods available in practice are as diversified in their nature as the genera of the material analyzed, every known qualitative reaction having been scrutinized with the object of pressing it into service, though often without success; and frequently when called on to analyze a substance, the chemist will find a purely physical method to give more accurate results and with greater expedition—in fact he at times has no alternative from the lack of a suitable chemical method.

Omitting details, the principal methods of analysis may be outlined as follows:—

A. GRAVIMETRIC METHODS.

1. By direct weight. In which each element is separated and weighed, either alone or more commonly in combination with another or others. Thus gold is always separated and weighed as an element, while zinc, difficult to obtain in the metallic form, is usually weighed in combination with oxygen as zinc protoxide, a simple calculation giving the weight of the metal in the oxide.

The routine is about as follows: the material to be analyzed is dried if necessary, and a small portion weighed and dissolved in water or an acid. Many substances require a special preliminary treatment before solution can be effected. A reagent is then introduced which will precipitate one of the components in an insoluble form, leaving the remainder in solution; this precipitate is caught on a paper filter, the clear liquid passing through, and after removing what solution adheres to it by washing with water, and the water by heating, it is weighed. Should the precipitate be of such a nature that it cannot be brought to a definite formula for weighing, it is redissolved and again

precipitated in a more suitable combination. The other constituents are in turn thrown out of the solution and weighed, as before described.

For example, of an alloy of tin, lead, and copper, a weighed portion is treated with nitric acid; the copper and lead dissolve as nitrates, while the tin is oxidized, mainly to insoluble hydrated metastannic acid ($H_2Sn_5O_{11}.4H_2O$). After filtration, the metastannic acid is freed from any adhering solution of the copper and lead nitrates by washing it with water, then heated until anhydrous, becoming stannic oxide (SnO_2), and weighed. As pure stannic oxide invariably contains a certain fractional part of its weight of tin, the product of the weight of the former by this fraction is the weight of the tin contained.

The filtrate and washings from the metastannic acid are united and mixed with an excess of sulfuric acid. The lead and copper nitrates become sulfates liberating nitric acid. The lead sulfate being insoluble precipitates; and filtering, etc., as before gives its weight and that of the lead by a similar calculation. From the filtrate from the lead sulfate the copper is precipitated as cupric sulfide by means of hydrogen sulfide; the precipitate loses on ignition one-half of its sulfur becoming cuprous sulfide (Cu_2S) and is weighed as such.

Other elements such as iron and zinc are generally present, but in minute proportions only. If it is desired to determine them, separate larger weights of the alloy are dissolved and treated according to special methods.

It must not be supposed that the actual analysis is as simple as would appear from the above. The metastannic acid always retains small amounts of copper and lead which must be reclaimed before the stannic oxide is weighed; the lead sulfate is somewhat soluble in nitric acid and water, so the former must be removed by evaporation, and dilute alcohol substituted for the latter; and precautions must be taken during the ignition of the copper sulfide to preserve it from oxidization by the air, and of the lead sulfate from reduction to the sulfide or metal by the carbon of the filter paper.

When a non-volatile stable compound is held in a solution it may be determined by evaporating the latter to dryness and weighing the residue; this presupposes that other solid compounds are either absent or volatilized during the evaporation or on heating the residue to a temperature insufficient to affect the first; but as these conditions can seldom be easily obtained the method is of limited application.

The Fire-assay. Applied exclusively to metaliferous ores, mattes and slags, and a few alloys, and principally to ores of gold and silver which contain but minute amounts of these metals disseminated through a silicious or earthy gangue. According to circumstances either the crucible or scorification process is employed.

Crucible Fusion. A fire-clay crucible contains a mixture of the ore with suitable fluxes like lead protoxide, sodium carbonate, etc., together with a half-gram or so of carbon. It is covered and heated to redness in a furnace, when the gangue of the ore unites with the fluxes forming a fluid slag. Simultaneously the carbon reduces its equivalent of the lead oxide to metallic lead ($2PbO + C + \text{heat} = 2Pb + CO_2$); the minute particles sinking through the mobile slag collect the gold and silver on the way, the alloy eventually gathering in a globule at the bottom of the crucible.

Scorification. When certain interfering elements, as arsenic, antimony or copper, are present in an ore the scorification process is usually preferred to the crucible fusion. The ore is mixed with metallic lead and a trifle of borax and heated in an open shallow clay dish (a scorifier) standing in a muffle (a thin semi-cylinder of fire clay) heated to whiteness in a furnace. The front of the muffle is open and allows free access of air to the scorifier, the oxygen

slowly converting part of the lead to oxide. The lead oxide gives up its oxygen to the arsenic, etc. The silica and bases of the ore, the oxide of lead, and the oxides of copper, etc. form a fluid slag floating on the surface of the lead-silver-gold alloy.

Cupellation. Subsequently the alloy is placed in a porous dish of bone-ash (a cupel) and heated in the muffle. The lead is converted to protoxide and partly escapes as fume and is partly absorbed by the cupel. The gold and silver are left as a metallic button since they do not oxidize in this process. They may be separated by 'parting' with diluted nitric acid which dissolves the silver only.

Electrolysis. Precipitation of metals through the agency of dynamic electricity has come into extended use during late years. Many metallic salts in aqueous solution are decomposed by a current of moderate strength and the metal deposited on an electrode connected with the zinc pole of a galvanic battery, while oxygen is liberated at the surface of another electrode connected with the copper pole.

In practice, the solution of the metal to be determined is held in a large platinum dish connected by a copper wire with the battery. In the solution is suspended a platinum plate, not touching the dish, also connected with the battery. After the current has passed for several hours all the metal will be found deposited on the dish as a coherent film; the weight is found from the increase in weight of the dish. A few metals like lead, manganese and thallium are deposited as peroxides on the positive electrode.

An old method, now supplanted by that described above, is the decomposition of a metallic salt in aqueous solution by a metal more electropositive than the one in solution, the latter separating as a powder or in a spongy mass, while an equivalent of the other metal dissolves. Thus, when a rod of zinc is introduced into a solution of copper sulfate, copper separates and zinc dissolves; similarly, lead is thrown out of a solution of lead chloride by metallic aluminum. The method is more appropriate as a means for the separation of a metal from others than for its determination.

Elementary Analysis. In an elementary or ultimate analysis of an organic or semi-organic body, the elements carbon and hydrogen are always to be determined, frequently nitrogen and oxygen, and occasionally sulfur, the halogens, etc. The principle on which hinges most of the methods is the conversion of the elementary constituents into gaseous compounds by burning in oxygen or otherwise; the mixture of resultant gases is passed through a series of tubes filled with different solid or liquid reagents. Each tube absorbs and retains one of the gases of the mixture, and being weighed before and after the operation, the difference in weight is that of the gas absorbed; or the contents of the tube may be treated to determine the gas by a gravimetric or volumetric process. From the weight of the gas — a definite chemical compound — may be calculated that of the element originally in the body analyzed.

For carbon and hydrogen a weighed portion of the substance is mixed with cupric oxide and placed in the middle of a long glass tube T, Fig. 1, whose rear end is closed. To the front end is attached two absorption tubes, A containing a hygroscopic solid (calcium chloride), to retain water, and B, a strong solution

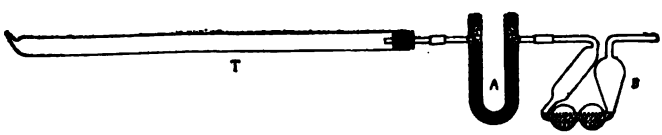


Fig. 1.

of a caustic alkali to combine with the carbon dioxide. On heating the tube the substance burns with the oxygen of the copper oxide, the water and carbon dioxide passing out through A and B. As the tubes have been weighed before the combustion, the increase in weight gives the amount of water and carbon dioxide they have respectively absorbed. To sweep out the gases remaining in the tube T, the posterior end is broken off and a current of pure air forced through the train.

Nitrogen is determined either by conversion to ammonia or by separation in the elementary form. For the former, the substance is mixed with sodium hydrate and lime and heated in a tube similar to the above; by the decomposition of water the nitrogen assimilates three atoms of hydrogen and becomes ammonia, which passing into a vessel containing a dilute mineral acid, combines with it. The ammonium salt is then determined gravimetrically or volumetrically. Or the substance may be decomposed by boiling with strong sulfuric acid, when the nitrogen becomes ammonia ($3C + N_2 + 3H_2O = 2NH_3 + 3CO_2$), this uniting immediately with sulfuric acid to form ammonium sulfate. The solution is diluted and made alkaline by sodium hydrate which combines with the sulfuric radical and liberates ammonia ($(NH_4)_2SO_4 + 2NaOH = Na_2SO_4 + 2NH_4OH$). The ammonia is distilled into hydrochloric acid forming ammonium chloride, and this compound treated by the usual process for the gravimetric determination of ammonium.

If, instead of soda-lime, the substance be heated with copper oxide, nitrogen is liberated along with the carbon dioxide and water generated; the mixture is passed into a gas-measuring tube standing over mercury. The water vapor condenses and the carbon dioxide is absorbed by an alkali solution, and from the volume of the remaining nitrogen is calculated its weight.

Oxygen is nearly always determined by difference, and sulfur, phosphorus, the metals, etc., by the usual gravimetric methods for inorganic bodies, previously destroying the organic matter by oxidation with nitric acid or a similar reagent.

2. BY INDIRECT WEIGHT.

By loss in weight. In a compound or mixture, one of the constituents may be volatile at a temperature insufficient to affect the others, so that its weight may be found from the decrement on heating. The method is appropriate for combined water and carbon dioxide in minerals; water of crystallization and combination of stable salts; etc. Small portions of organic in inorganic matter may be burned away by ignition in a current of air or oxygen.

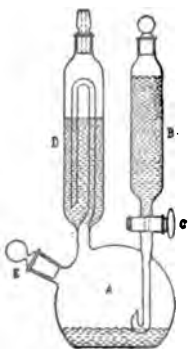


Fig. 2.

A mixture of several bodies may be treated by a reagent which will dissolve one body leaving the remainder practically unacted on, the difference between the original weight and that of the residue being the weight of the body dissolved. Thus, copper is dissolved from associated carbon, alumina, etc., by a solution of ferric chloride; silica from metals by hydrofluoric acid; gold from quartz and silicates by bromine water.

The radical of a mineral acid may displace that of a weaker volatile acid, and the weight of the latter found by the loss in weight of the mixture. For example, sulfuric acid acts on a carbonate to liberate carbon dioxide; as $MgCO_3$ (magnesium carbonate) $+ H_2SO_4 = MgSO_4 + CO_2 + H_2O$.

The determination is made by means of an apparatus

termed an alkalimeter, one of the many forms being shown in Fig. 2. The magnesium carbonate is weighed and introduced into the light glass flask A together with a little water. The tube B is filled with dilute sulfuric acid which may be run into A by opening the stop-cock C; the exit tube D contains concentrated sulfuric acid to retain water from the gas passing out through it. The flask is weighed and an excess of acid run into A from B; as the carbonate dissolves, the carbonic acid bubbles through D leaving it as anhydrous carbon dioxide. When action has ceased the solution of magnesium sulfate is boiled, and a current of air drawn through the apparatus to sweep out the last traces of the gas. Finally the flask is weighed, the loss from the former weight being carbon dioxide.

From the weight of another element or radical with which it combines. If two atoms or radicals a and x unite to form the molecule $a\,x$, it follows that if the weight of a is determined, the corresponding weight of x may be calculated from their combining weights. For example, one way of determining ammonium (NH_4) is to combine it with chlorine and platinum to form the compound ammonium platinic chloride $(NH_4)_2PtCl_6$. On igniting this compound all the elements except platinum volatilize, and from the weight of the residual platinum may be calculated that of the ammonium, the ratio being as 194.9 (atomic weight of platinum) to 36.144 (twice the molecular weight of ammonium).

A product of the reaction between the body to be determined and a reagent may be weighed or measured, and the weight of the body calculated therefrom.

(1) The product may be determined in the same solution in which the reaction takes place; thus, a neutral solution of cadmium sulfate treated with hydrogen sulfide yields sulfuric acid and a precipitate of cadmium sulfide; the free sulfuric acid is then determined by a volumetric process and the weight of cadmium calculated.

This principle is extended in the following example.* Let it be required to determine the percentage of phenol in a commercial sample; a weighed quantity of the sample is treated as follows: —

A. On evaporation with an excess of concentrated sulfuric acid phenol is converted into soluble (para) phenolsulfonic acid.

$$2(C_6H_5OH) + 2H_2SO_4 = 2(C_6H_5HSO_4) + 2H_2O \quad \ldots\ldots (1)$$

Phenol — Phenolsulfonic acid

B. The solution is diluted with water and (insoluble) barium carbonate stirred in; the phenolsulfonic acid combines with barium to form *soluble* barium phenolsulfonate.

$$2(C_6H_5HSO_4) + BaCO_3 = Ba(C_6H_5SO_4)_2 + H_2CO_3 \quad \ldots\ldots (2)$$

Phenolsulfonic acid — Barium phenolsulfonate

At the same time the excess of sulfuric acid necessarily employed in A reacts with barium carbonate to form insoluble barium sulfate.

C. The precipitate of barium sulfate mixed with the excess of barium carbonate is filtered off, and to the clear filtrate, containing only barium phenolsulfonate, is added an excess of sodium carbonate, the metathesis giving *soluble* sodium phenolsulfonate and *insoluble* barium carbonate.

$$Ba(C_6H_5HSO_4)_2 + Na_2CO_3 = Na_2(C_6H_5SO_4)_2 + BaCO_3 \quad \ldots\ldots (3)$$

Barium phenolsulfonate — Sodium phenolsulfonate

The liquid is filtered and the barium carbonate weighed.

D. From the weight of the barium carbonate is calculated that of the barium it contains; from the weight of barium, the weight of the rest $(C_6H_5SO_4)_2$ combined with it by equation (3); from the $(C_6H_5SO_4)_2$, the weight of the phenolsulfonic acid by equation (2); and from the phenolsulfonic acid, by equation (1), the weight of phenol generating it and the percentage of phenol in the sample (page 176).

(2) If a product of the reaction is an insoluble gas it may be carried from the solution to a suitable receiver and there weighed or measured. Thus,

* Druggists Circular, 1896—158.

when aspartic acid is boiled with a solution of nitrous acid there is evolved nitrogen ($H_2C_4H_5NO_4 + HNO_2 = N_2 + H_2C_4H_4O_5 + H_2O$); the nitrogen is passed into a graduated gas-tube and the volume measured, one-half coming from the aspartic acid and one-half from the nitrous acid.

Or instead of directly weighing or measuring a gas, it may be passed through a solution of a reagent and an insoluble product of this second reaction weighed. Thus, ferrous sulfide with hydrochloric acid yields gaseous hydrogen sulfide; the latter is passed through a solution of silver nitrate and the precipitated silver sulfide filtered out and weighed.

Volumetric Analysis. This designation is commonly applied to the following described process though it would appear to belong more properly to the methods of Division 3, below.

In every metathesis the rearrangement of the molecules takes place in a fixed ratio, and from the general equation $AB + XY = AX + BY$, if the weight of the element or radical A or B is known, the weight of X or Y can easily be calculated.

In volumetric determinations small weighed quantities of AB are added in succession to a solution of XY until the reaction is just complete, this point made manifest by some visible change in color of the solution or otherwise. It is more convenient, and, with a few exceptions, the rule, to employ a solution of AB of known strength, reckoning the weight of AB used from the volume of the solution required — hence the name of "volumetric" analysis.

For example (taking the simplest of the various modifications), the percentage of silver in a coin is to be determined. Exactly equal weights of the coin and of pure silver are separately dissolved in nitric acid; into the first solution is cautiously poured from a graduated tube a dilute solution of sodium chloride, forming a white precipitate of silver chloride. On vigorously stirring the solution the precipitate collects into one mass leaving the liquid clear. Successive additions of the salt solution are made until a cloud ceases to form, showing that all the silver has combined with chlorine. The volume of the salt solution used is noted, and the above process repeated with the second solution. The proportion is then solved —

Volume of salt solution required to precipitate the pure silver: volume required for the coin:: weight of pure silver: weight of silver in the coin.

If we ascertain that C volumes of the salt solution precipitates D grams of silver, then one volume precipitates $\frac{D}{C}$ grams, and we have a *standard solution of sodium chloride;* the number of volumes used for any alloy multiplied by this fraction giving the weight of silver contained.

By difference. When the sum of the weights of all the constituents except one is subtracted from the weight of the substance taken for analysis, or the sum of their percentages from 100 per cent, the determination of the one constituent is said to be made "by difference."

3. BY VOLUME.

Gasometry. To analyze a mixture of gases, a convenient volume is brought into a long graduated glass tube supported in a vertical position, the upper end being sealed while the lower end is open and immersed in a vessel of mercury. The volume of the gas being noted, a solid or liquid reagent capable of absorbing one gas only is introduced and after a time withdrawn, when the diminution in volume shows the proportion of this gas in the original mixture. The other gases are successively eliminated in the same manner, except nitrogen, hydrogen, and some hydrocarbons for which no absorbent is available.

Hydrogen is determined by introducing a measured volume of pure oxygen and kindling the mixture by an electric spark; the water formed by the combination of these elements condenses, and the diminution of the total volume is the volume of the hydrogen. The same plan is pursued with gaseous hydrocarbons, their combustion producing carbon dioxide and water; the former is then removed by a suitable absorbent. Nitrogen is determined by difference.

A gaseous constituent of a solid or liquid may be evolved by displacement by a stronger radical; as carbon dioxide from carbonates on solution in a mineral acid; the nitrogen of urea set free by sodium hypobromite; etc. The product of the decomposition is passed into a gas-measuring tube and its weight calculated from its volume.

The weight of a liquid suspended or in contact with another may often be found more conveniently by measuring its volume than by actual separation and weighing. In computing the weight the specific gravity of the liquid is a factor. A simple illustration is the well-known method of testing milk by the "creamometer"; a tall, graduated jar is filled with milk, and when the fat-globules have risen to the surface the volume of cream is read on the graduations of the jar. The fusel oil in alcoholic liquors is estimated by mixing the liquor with a measured volume of chloroform; the chloroform extracts the oil with a proportional increase in its volume. Chloral hydrate mixed with a solution of sodium hydrate decomposes into soluble sodium formate and insoluble chloroform; the volume of the latter is a function of the weight of chloral reacting.

The volume of a precipitate formed in a solution under fixed conditions of temperature, dilution, agitation, and time of repose, bears a fairly constant ratio to its weight. In methods based on this principle, not the actual volume of the precipitate is measured but the space it occupies after settling interspersed with the surrounding liquid. But from the difficulty of adhering strictly to the conditions prescribed and through unavoidable errors in measuring, the method is limited to the determination of such elements as form but a small proportion by weight of the precipitate or of the substance analyzed, where these sources of inaccuracy have the least effect.

One application is for the approximate determination of phosphorus in steel.* One gram of the metal is dissolved in dilute nitric acid in a pear-shaped glass bulb, Fig. 3, whose lower extremity is narrowed into a nearly-capillary graduated tube A. The phosphorus being oxidized completely to phosphoric acid, a solution of molybdic acid in ammonium nitrate and nitric acid is added, producing a dense, finely granular precipitate of ammonium phosphomolybdate. The precipitate slowly subsides into A or is quickly forced in by whirling the bulb in a centrifugal machine. In the latter case each graduation of A represents .01 per cent of phosphorus in the steel.

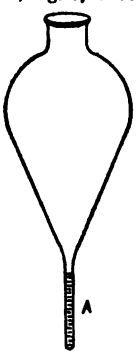


Fig. 3.

4. BY THE EXTENT OF SOME SPECIFIC PROPERTY.

Colorimetry. When a substance or one of its constituents gives a colored solution, the intensity of the color is assumed to be in a direct ratio to the amount of substance dissolved; and in two solutions of equal depth of tint, the weights of substance dissolved are in direct proportion to the volumes of the solutions, the known weight of one serving to establish that of the other.

The methods are only comparative and for several reasons are best suited for technical work where strict accuracy is not essential.

* Zeits. angew. 1889—688.

The most common of the methods is to prepare a solution, in water or other medium, of a certain weight of the sample to be tested, and pour it into a long graduated test-tube. Into another tube of the same diameter is placed a solution containing a known weight of the pure chromogenous constituent of the sample, or of a body containing a known proportion of it. The darker solution is diluted with water until the tints of the two have the same intensity, and a calculation from the weights employed and the respective volumes gives the percentage of the constituent in the sample.

By divergent values of a constant. When two allied bodies possess a common physical characteristic to an unequal extent or chemically react with a third body in dissimilar ratios, the constant of a homogeneous mixture of the two lies between those of the constituents, its distance from either being a function of the proportion of the constituents in the mixture. In general, this proportion may be computed from the simple equations, $X + Y = 100$, and $aX + bY = 100d$; whence $X = 100\,\frac{d-b}{a-b}$ and $Y = 100\,\frac{d-a}{b-a}$ in which X is the percentage of one constituent; Y, that of the other: a, a given constant of X; b, of Y; and d, of the mixture.

For example, when linseed oil is digested under certain conditions with an excess of iodine it combines with about 175 per cent of its weight of the halogen, while cottonseed oil combines with only 108 per cent. If it be proved by qualitative tests that a sample of the former oil is adulterated with the latter, the proportion of each oil may be calculated after finding the percentage of iodine taken up by the sample—should it be, for example, 161.6 per cent, the proportion of cottonseed oil in the mixture is 20 per cent.

It is clear that this method is not applicable where the constant of the mixture is affected by reactions consequent on the bringing together of the constituents, and that the degree of accuracy that can be attained in any determination is dependent on the extent of the disparity of the constants and the exactness with which they can be — or have been — determined Confidence in the deduction is enhanced if the results obtained by two or more constants agree within reasonable limits, when the average of these results will probably closely approximate the true percentage.

Of a variety of constants that may be employed, such as melting and solidifying temperatures, refraction of light, rotation of polarized light, solubility, etc., one in particular is in extended use, namely specific gravity. It may be applied to a mixture of solids, as alloys and amalgams; to gases, as for the determination of carbon dioxide in a chimney-gas; and especially to liquids. It must be observed, however, that the volume of a mixture is often not so great as the sum of the volumes of the constituents, and in this case, of course, the above formulae will not apply. Where such is the case, tables may be drawn up from data obtained by mixing the pure constituents in progressive ratios, carefully noting the densities of the mixtures, and supplying intermediate values by interpolation; for liquids, tables may be fitted to special hydrometers (page 159), showing at a glance the proportion of one constituent, and by their aid results quite accurate enough for most technical work can be had immediately and with a minimum of labor.

Aqueous solutions of certain bodies deviate the plane of a ray of polarized light according to a specific coefficient of rotation and to an extent commensurate with the concentration of the solution. Of the optically active bodies, some turn the plane to the right (dextro-gyrate), others to the left (laevo-gyrate). The extent of the rotation is observed by an instrument known as the polariscope. Of the many forms all agree in having four principal parts — a calcite prism to polarize a beam of light; a long metal tube with glass ends

filled with the solution to be tested and through which the polarized beam passes; an arrangement of prisms and lenses to exhibit to the eye the extent of the rotation; and a scale for measuring the rotation. The angle of deviation is shown in one form of apparatus by the identity in color and tint of two luminous semi-circles, in others by the position of black bands on a white field or their disappearance, etc. The polariscope is used for the determination of alkaloids and essential oils, in pathological examinations, and extensively for cane sugar and glucose.

Aqueous solutions of many salts refract a ray of light, the angular displacement increasing with the proportion of the solid in solution. Alcohol, albumen, the oils, etc., also possess this property to a greater of less extent. The deviation is measured in an instrument known as the refractometer.

Attempts have been made to employ the spectroscope, so useful in qualitative analysis, for quantitative examinations of alloys, dye-stuffs, and other materials. Various other principles have been proposed for use in special cases, as the difference in height to which liquids ascend in capillary tubes, the vapor tension of volatile liquids, electric conductivity, viscosity, melting, freezing and boiling points, etc.

Separation by mechanical means comprises sifting through various sized meshes, applied for example in the separation of fibrous from granular particles; elutriation, in floating a light mineral in fine powder from one much heavier; extraction of particles of iron by the magnet from non-magnetic matter, e. g., boneblack; vanning, etc.

CHAPTER 2.

SAMPLING—PREPARATION OF THE SAMPLE FOR ANALYSIS.

The market value of a raw material or commercial product is now commonly decided on the basis of its analysis, and some judgment and experience are called for to withdraw a representative portion of a suitable size in such a manner as to preclude any suspicion of discrimination or selection, either unconsciously or fraudulently, of a quality superior or inferior to the average of the original. Where the material is a solid in the form of small particles or powder, fairly homogeneous and well mixed, and with liquids and gases the operation is mechanical only, and the proportion by weight or volume that the sample bears to the original may be comparatively small. But for a heterogeneous material where it is impracticable to pulverize the whole, only a large and judiciously chosen sample is of any value; examples are found in some ores, made up of large and small lumps and coarse and fine powder all differing in composition—perhaps the interior of a lump differing from the exterior; vegetable products where the granular parts and fiber contain unequal amounts of some active principle; photographic wastes; paint-skins; scrap metal; waste manufactured rubber; etc., etc.

In withdrawing a representative from a commercial article prone to undergo spontaneous change or be altered by variations in temperature, contact with air or moisture, or partial volatilization of a constituent, it is important that the sample should be divided between the buyer and seller and analyzed without delay. Changes in composition to the detriment of the quality and value are likely to take place more rapidly in the original packages exposed to air and moisture than in the sample kept in a closely stoppered bottle; and if the analyses accord to the satisfaction of both parties to the transaction, there will be less difficulty in reaching an agreement as to the extent of any depreciation of the original should the sale or transfer be delayed.

The following examples illustrate the general procedure to be followed in sampling commercial articles.

Car lots of ores or like materials are often sampled in this way: The surface is divided into squares by equidistant perpendicular lines one or two feet apart, and at each intersection a spadeful is taken out, or if the intersection falls at a lump, a fragment is broken away. Uniting these, the whole is weighed, dried at 100° and again weighed to show the proportion of moisture contained, then crushed to pass a screen of say one-quarter inch mesh. The pile is spread out in a large circle and two opposite quadrants rejected, the remainder crushed somewhat finer and again halved, and so on, the size of the fragments and the weight of the sample being correspondingly reduced until only a few ounces of fine powder remain.*

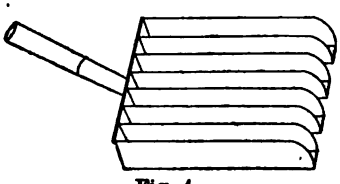


Fig. 4.

* School of Mines Quart. 1892—364.

Instead of dividing the piles as described, some prefer to transfer a half with the sampling- or split-shovel, Fig. 4, a series of alternate rectangular cups and spaces. A device for dividing the final powder into four parts is shown in Fig. 5, the funnel A being moved rapidly to and fro over the distributer B. It is the custom for the purchaser to retain one bottle for analysis, the second is sent to the shipper, the third to a referee, and the fourth sealed and preserved for emergencies.*

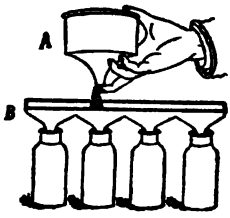


Fig. 5.

In sampling ores, coal, limestone, etc., from stock-piles or cars it is often assumed that the surface represents the interior, but if at all doubtful, it is the safer plan to dig in so far as to cut through all the layers formed as the ore was dropped on the pile or loaded into the car. This applies also to ensilage, fodder, haystacks, etc.

During the unloading of a cargo of ore or like material, a small portion of every fifth or tenth barrow furnishes an unexceptionable sample. In a mine or quarry the face of ore or rock is marked off into squares of suitable dimensions and a piece picked at each intersection — always exercising caution against the possibility of the mine being "salted."

In sampling commercial metals, from bullion and bars little cylinders are cut out with a punch. Ingots, pig iron, and metal shapes are drilled through in several places and the drillings well mixed to annul any segregation or non-uniformity of structure, unless it is desired to ascertain the existence of this condition.

The fairest sample is obtained by remelting and dipping out a small ladle-ful, which, after solidification, is drilled or pulverized. If this is impracticable, a fair representative may perhaps be cut from just below the surface where immediate solidification has checked segregation. From a pig or bar, a thin section perpendicular to the axis; or fine drillings from several holes as deep as possible and well mixed, best by drilling out a large quantity and subdividing as before described. Easily fusible alloys are previously melted and cast into ingots, stirring rapidly while cooling to promote homogeneity.

The uniform distribution of the impurities in the metals of commerce has often been the cause of discrepancies between analyses, resulting in friction and controversy. Admitting an originally perfect mixture of the molten metal, by segregation an undue proportion of the impurities pass toward the median line of an ingot and rise near to the upper end where a "spot" may form charged with double or triple the impurities held by the metal nearer the surface.† Obviously duplicate determinations of any impurity will not agree should one determination be made on borings cut from near the surface, the other from further in, or both from an imperfect mixture of the two.

When a molten metal is to be sampled, as iron from a cupola, it is best to allow a thin stream to fall into water, where solidification takes place so rapidly that but little segregation can occur, and there is consequently less danger of a non-uniform sample. The chilled spheroids cannot be drilled or filed, but are so brittle that they may easily be crushed to powder. For melted slags a cold iron rod is thrust in and quickly withdrawn; as the chilled coating of adhering slag is amorphous in structure its powder is more readily attacked by acids (an advantage in the analysis) than if the slag were allowed to cool slowly and become crystalline.

Recent vegetables, roots and seeds are rasped, divided in a tobacco-cutter,

* Trans. Amer. Inst. Min. Engrs. 1891—155.
† Journ. Anal. Chem: 2—70.

or contused in a lignum-vitae or boxwood mortar. If the sap or juices are to be examined, the vegetable is passed through a pair of rolls at a suitable pressure or expressed in a fruit-press or small cider-mill. Sugar beets are pierced with a rapidly rotating hollow drill roughened at the point, withdrawing the interior in the form of pulp. Dyewoods are sawed through transversely to the fiber and the sawdust mixed and "quartered" as described for ores. Of the softer drugs like opium received in case lots, from every tenth lump is excised a cone whose apex is the center of the lump, and from each cone a narrow sector; the sectors are worked into one homogeneous mass by the fingers, and slices taken from it for the analysis.

For the valuation of oil-cake and solids marketed in similar shape, a narrow strip is cut from one corner to the corner diagonally opposite, or a whole cake is broken in half and a strip cut from each half. Packages of butter, cheese, bins of grain, bags of ground fertilizers, etc., have a long tube of thin metal passed entirely through the package cutting a cylinder which is assumed to be representative. With shipments of tallow or other solid fat, a core is cut from each cask, and from the cores weights proportional to the weights of the casks from which they were taken; these are melted together at a low heat and constantly stirred during cooling, and from the granular mass is withdrawn the portions for analysis. Arranged to retain a liquid, the tube becomes a "thief" used for abstracting oils, liquors, etc., from barrels and tanks.

Viscous liquids are drawn by a glass syringe with a large orifice; when samples from several barrels are to be united to form a composite one, the syringe can be graduated so that a volume proportional to the weight of the contents of each barrel may be included in the mixture. Packages of liquids containing insoluble suspended matter, such as paints and semi-solids generally, are transferred entire to a large dish, well mixed, and suitable portions withdrawn for analysis before any deposition can take place. The importance of thoroughly mixing a sufficiently large quantity of a heterogeneous solid before dividing down to a sample applies equally to liquids that stratify on standing or deposit a sediment. Slimes are passed through a filter-press and a section cut from each cake; the sections are together rubbed up with water and the liquid filtered, and from the resulting cake is cut a section for assay.

For spring or other natural waters, an empty stoppered bottle is submerged to the proper depth, the stopper withdrawn and reinserted when the air has been displaced by water. The excess of carbonic acid in aqueous solutions supersaturated under pressure, as table waters, beers, or sparkling wines, is drawn slowly and without loss through a champagne tap or its equivalent, passing through a rubber tube into the solution for its absorption.

Gases diffuse one into another so readily that after contact for a reasonable time any portion of a mixture represents the whole. With heating and illuminating gases, the conducting pipe may be tapped at any point and the gas drawn through a dry meter into a gasometer or directly through the train of apparatus for its analysis. A simpler plan is to connect to a branch of the gas-pipe a large syringe provided with a three-way stop-cock at the orifice, and fill it by retracting the piston, this appliance avoiding any contact of the gas with water and absorption of a soluble constituent like carbon dioxide or hydrogen sulfide.

For the determination of minute proportions of a gas in a mixture, as carbon dioxide in air, a large volume is passed through an absorbing fluid contained in tubes of a special design, then through a gasmeter to learn the volume transmitted. When the average quality of a gas generated in a furnace or producer in a given length of time — say 24 hours — is to be determined, a

large aspirator is filled with mercury or water and the tap at the bottom opened only so far that the mercury will be entirely withdrawn in the specified time, the gas entering through a capillary tube as the mercury flows out.

Schloessing's apparatus for the determination of carbon dioxide in a soil is a steel tube of a bore of two millimeters, pointed at the lower end. The bore is closed by a wire of slightly less diameter, and the tube driven into the soil. The wire is withdrawn and the gases aspirated into a bulb-tube by means of a mercury aspirator.

During the manufacture of certain commercial products samples may have to be taken out periodically to show the progress of the chemical reaction or to indicate its completion. Small ladles of iron are dipped from a furnace making open-hearth steel to find the rate at which the carbon or phosphorus is being removed from the bath; hourly samples of the mixture of soap-stock and alkali from the autoclave to ascertain how rapidly the saponification is progressing; gas from a gas producer for the variation in the ratio of carbon monoxide to carbon dioxide; etc.

In technical work there is sometimes required the analysis of an article from which only a small part can be removed for a sample, such as a roll of paper, a tanned hide, or a sheet of metal bearing a "coupon." Here deductions from the results of analysis must be drawn mindful of a possibility of the non-homogeneity of the original.

With large lots of manufactured articles, or where it is impracticable to open all original packages, from one to ten per cent of the lot is picked at random and assumed to be representative. Obviously this plan is unsatisfactory at best, though often the only one possible, since an unscrupulous dealer will often take advantage of the opportunity to include a small proportion of an inferior quality, relying on the improbability of any one of these entering the number picked for the test.

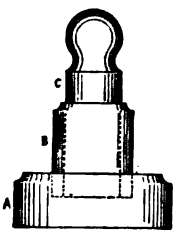


Fig. 6. 1/3

Mechanical sampling. Several machines have been invented for sampling large consignments of ore or matte in powder or for liquids. They are so constructed that the entire lot falls in a continuous stream through an orifice in an elevated bin to another bin some distance below. A suitable mechanism cuts out for the sample a section of the stream continuously, or the whole stream is momentarily diverted at regular intervals of time.

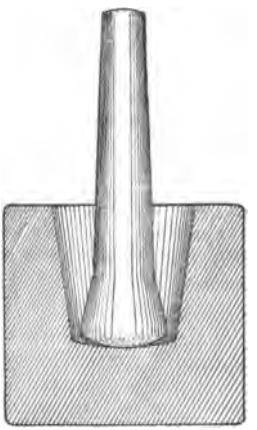


Fig 7. 1/4

Pulverizing. Easily soluble compounds and crystalline salts in general need only be coarsely powdered for the removal of any foreign matter, moisture in the lammalae, or inclosed mother-liquor, and for convenience in weighing. Minerals, less easy to dissolve, must be ground to a fine powder. They are broken into small fragments, and clean pieces freed from gangue by picking out under a magnifying glass, or by separation with a solution of intermediate density. The fragments are crushed in a diamond steel mortar, Fig. 6. In a cavity in the hardened steel base A stands an iron collar B containing the fragments to be pulverized; the

pestle C slides loosely in the collar and is struck by a hammer until they are reduced to granules. Fig. 7 shows in section a mortar made of hardened steel used for powdering white iron and similar substances.

Fig. 8.

Small parcels of ores may be broken down in an iron mortar, both mortar and pestle of a hard, tough grade of cast iron, Fig. 8. The mortar should have a solid support, best the upper end of a wooden post sunk several feet in the earth, and the manipulation of the pestle is less laborious when it is suspended at the end of a spiral spring hung from the ceiling.

Ores and other hard materials in lumps are quickly reduced to a moderately fine powder in a hand-crusher of which several styles are on the market. One is shown in section in Fig. 9. The ore is fed between the serrated jaws A and B. The former is fixed to the frame of the machine, and the latter held by the rod E bearing on the rubber spring F, against two pivotal bearings C and D. C is supported by the frame, and D presses against the short arm of the bent lever H. The lever oscillates on J, and the long arm is actuated by the cam G turned by a hand-wheel. As the cam rotates, the jaw B swings toward A and crushes the ore between them, and as it recedes the powder falls into a pan below. For large lots of ores a rotatory crusher is more suitable, and a ball-mill has some advantages for certain materials.

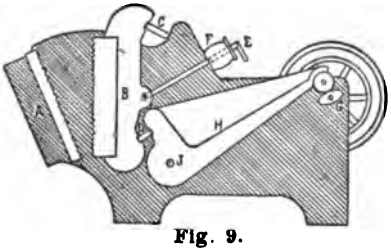


Fig. 9.

Shavings of iron may be cut from a steel or iron mortar by the harder minerals, to be removed by stirring the powder with a magnet; but if a magnetic mineral is to be pulverized some other means of extraction must be used, such as dissolving out the iron with a solution of some chemical that will not affect the mineral. For the assay of ores other than iron, the presence of such a relatively small amount of iron is of less consequence and may safely be disregarded.

Very hard anhydrous minerals may be broken up by heating to redness and quenching in water, provided that the composition is not changed by this operation.

A metal or alloy dissolving readily and *completely* in an acid may be weighed in the form of one or more pieces as it is often difficult to subdivide without contamination by foreign matter from the file or other instrument. If brittle it may be powdered in the same way as a mineral, but if malleable, as is more often the case, is rolled or hammered into a sheet and cut by shears into strips of a convenient weight, or, if very soft, may be whittled by a knife or chisel.

A metal may be finely divided by alloying it with a large proportion of another and dissolving out the latter with an acid which will not attack the former; as platinum with zinc, the zinc extracted by nitric acid leaves the platinum as a powder far more readily dissolved in aqua regia than if in the massive form.

Soft and tenacious solids and semi-solids are difficult to pulverize and mix uniformly, and this operation may be facilitated by the incorporation of a harder substance, like sand or asbestos, so chosen that it shall not interfere in the analysis. This is called "pulverizing by intervention."

Mortars. The powder is finally passed through a sieve having not less than

forty meshes to the linear inch; if an ore is being pulverized, or in fact any mixture, *every particle* must go through, for it is evident that what remains on the sieve contains an undue proportion of the harder and tougher particles, or those of a malleable or fibrous character. The resulting powder is to be thoroughly mixed before dividing down.

A few grams are then ground to the proper degree of fineness in an agate, wedgewood or porcelain mortar. The first named, Fig. 10, is to be preferred, as by reason of its flinty nature it suffers less from abrasion by a hard mineral than either of the others and consequently the powder is impurified to a less extent. In selecting one, the interior should be examined for perceptible cracks and fissures apt to harbor a little of one powder to contaminate the next one ground. It should be slightly roughened before using by grinding a little emery flour, and can be cleaned in the same way. For greater stability it may be imbedded in a hardwood block.

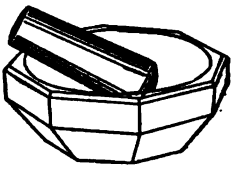


Fig. 10. $^1/_4$–$^1/_6$

The pestle should be long enough to be comfortably grasped or be set in a wooden handle, and its grinding face have a convexity of somewhat less radius than the interior of the mortar. It is manipulated with a rubbing motion only, as pounding is less effective and liable to chip its edge or crack the mortar, for it is well to remember that banded agate is quite brittle and easily fractured by a slight blow. The powder must be occasionally brushed down to the center of the mortar during the grinding, that every part receive its share of the trituration.

Wedgewood and porcelain mortars will answer for the softer minerals such as talc or graphite, crystalline salts and organic substances, while those of glass are only suitable for mixing powders and like operations. The 'buckingboard,' Fig. 11, is used in technical work for rapidly breaking down ores. It is a hard steel plate, A, with a muller, B, having a curved base and provided with a long handle. The grinding is done by running the muller back and forth with a slight oscillatory motion, at the same time pressing it down with the left hand.

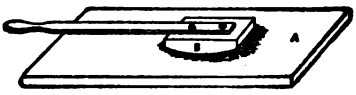


Fig. 11. ($^1/_{16}$)

Grinding by power.* Pulverizing large amounts of ore by hand is rather slow and tiresome, and machines are in use for this purpose actuated by pulleys from a shaft or by a water-motor. In one machine the pestle is hinged at the center of the arc of the concavity of the mortar and oscillates across it, both the mortar and pestle revolving slowly at the same time. The mortar is supported on one end of a lever, and is pressed up against the pestle by a weight at the other end.

In a simpler contrivance the mortar is stationary and the grinding is done by hand in the usual way with the difference that the hand grasps a sleeve within which the pestle is rapidly rotated by means of a flexible shaft joined to the upper end.

Sifting — Levigation. The fineness to which the pulverization is to be carried is dictated mainly by the solubility or ease of decomposition of the substance. Chalk, for example, dissolves in acids so readily that it is ground merely to obtain a homogeneous mixture of the mineral and its impurities, while on the other hand, minerals like chromite, the titanic acid and alumina families, cassiterite, and zircon are so dense and refractory that their trituration can scarcely be prolonged to an unprofitable extent. But, as a rule, a powder may be considered sufficiently fine if no grittiness is observed when rubbed between the fingers.

* Chem. News, 1888–2; Blair, Chem. Anal. of Iron, 13; Journ. Anal. Chem. 2–81.

A uniformly fine powder results from sifting through some thin closely woven fabric, such as bolting-silk. Another plan is that of levigation, stirring the powder into an inactive fluid and after a time decanting the liquid holding the finer particles in suspension, these subsiding after the liquid has been allowed to stand undisturbed for some time. Unfortunately but few powders are entirely unaffected by water or other liquids, which frequently acts as a solvent to a degree that would not be expected, and the levigated powder differ considerably from the original by reason of the constituents dissolving to an unequal extent. But, on the whole, it is seldom that a thorough grinding in an agate mortar will not suffice for analytical purposes without need of recourse to either of the above expedients.

PREPARATION OF THE SAMPLE FOR ANALYSIS.

When the composition of a definite chemical compound is to be ascertained for the deduction of its formula, entire freedom from other bodies must be assured by qualitative tests, and impurities, if detected, removed by a suitable treatment chosen according to the nature of the substance and the impurity.

Crystalline salts are purified by dissolving in hot water or other solvent to the specific gravity suitable for crystallization, filtering as hot as possible through paper or asbestos, and allowing to cool during continuous stirring that only small crystals may be deposited. Precautions must be taken with a double salt that the product shall not partially dissociate into the simple ones composing it. The crystals are dried by pressing between filter paper, or if decomposed by organic matter, on a porous tile or in a funnel connected with a vacuum pump; more quickly by inclosing them in a perforated basket of porcelain or wire gauze and revolving it in a centrifugal machine.

When a salt is easily oxidized by exposure to the air or otherwise affected on evaporation, a better plan is to precipitate it in the crystalline form by reducing the solvent capacity of the menstruum, as by the addition of alcohol or an acid to an aqueous solution, or ether to an alcoholic one. Thus a solution of commercial ferrous sulfate always contains more or less ferric sulfate; the addition of alcohol precipitates only the former, as the latter is comparatively quite soluble in dilute alcohol.

An impurity in a salt may also be eliminated from its solution by precipitation with an appropriate reagent, provided that the reagent has no action on the salt and that its excess can easily be removed by evaporation or otherwise. An expedient often resorted to is that of replacing the base of an impurity by the base of the salt to be purified, the former being precipitated. Thus if into a solution of zinc sulfate containing ferric sulfate, is stirred a little zinc oxide, all the iron will be precipitated as ferric hydrate —

$$Fe_2(SO_4)_3 + 3ZnO + 3H_2O = Fe_2(OH)_6 + 3ZnSO_4.$$

and it is obvious that zinc oxide will yield an iron-free solution if treated with dilute sulfuric acid in quantity insufficient for entire solution.

Dialysis may be resorted to with advantage to free an inorganic salt from organic impurities of such a nature that only repeated recrystallization would eliminate them, or to separate a colloidal compound from a crystalloid.

A solid volatile on moderate ignition, as indigotin, camphor, or benzoic acid, is purified by the process of sublimation. After drying the substance in the desiccator it is gently heated in a porcelain dish covered by an inverted funnel in which the fume condenses, or by inclosing it between two watch-glasses and heating the lower. Metals of comparatively low boiling points, like cadmium and zinc, can be distilled in vacuo leaving a residue of whatever is not volatile at the temperature employed.

A liquid is freed from suspended matter by subsidence and decantation or filtration through paper or felt, and from dissolved impurities by lowering the temperature to such an extent that they separate in the solid state, by extraction with another immiscible liquid, by treatment with a strong acid to carbonize organic matter, etc. Optically active liquids or solutions are clarified for examination in the polariscope or refractometer by basic lead acetate, or digestion with animal charcoal, fuller's earth, talc, or a mixture of wood-meal and finely powdered infusorial earth.

Volatile liquids are distilled from non-volatile matter and the vapor condensed (page 62), after digestion over some hygroscopic solid if water is to be eliminated. Repeated fractional distillation serves to isolate one of a mixture of volatile liquids or a fraction of a homologous series coming over between certain specific temperatures.

A gas is transmitted into the apparatus for analysis through a series of wash-bottles or tubes containing granular solids to absorb water. From gases produced or used in technical processes, tar, soot and dust are retained when the gas is conducted through a column of some closely packed fibrous material; otherwise the gases are analyzed as obtained or delivered to the consumer.

Various other modes of purification may be adopted as circumstances admit; for the metals and other elements, elaborate directions will be found in the literature on the determination of their atomic weights.

Drying the sample. The amount of moisture condensed in a porous body exposed to the air varies with the atmospheric temperature and humidity, so it is the rule to dry all powders previous to their analysis and preserve them in tight receptacles until actual work is begun. The point at which a substance is altered or decomposed limits the degree of heat to be applied; moisture, however, should not be confounded with water of crystallization or constitution, neither of which must be disturbed in the drying, their removal being usually considered as constituting a part of the analysis proper. With some few organic bodies, exposure to a heat above ordinary (or freezing), causes a marked reduction in solubility, and such are analyzed as received, the water determined in a separate portion and the percentage calculated. An instance of the mal-effect of prolonged drying is found in linseed cake, the amount of linseed oil soluble in ether being largely diminished.

Minerals, ores, and commercial raw materials and products in general, after having been sampled and pulverized as described in the preceding pages, need only a removal of the hygroscopic water to be ready for analysis. The drying is often omitted, as when the object of the analysis is to decide the value of a material in the condition as found on the market, but it is to be remembered that any extensive preparation for analysis in the way of grinding or mixing gives an opportunity for either evaporation or absorption from the air of a considerable amount of moisture with a correspondingly inaccurate result. It is better therefore to determine at once the percentage of moisture in the material, thoroughly dry the portion taken for analysis, and calculate the results obtained to the undried material (page 177).

Certain amorphous bodies, cellulose for example, appear to have a normal water-content, and frequently the analysis is expressed on this basis. Aerhydrous bodies, when only coarsely ground may not part with all the water they contain at a temperature of 100°, but if in a fine powder lose it at ordinary temperatures when dried in a desiccator over sulfuric acid. Soils are analyzed

in an air-dried condition, that may only be arrived at by several days' exposure in thin layers.

A. Crystalline salts are coarsely powdered and pressed between bibulous papers until the crystals show no tendency whatever to adhere together, deliquescent and efflorescent salts to be handled as expeditiously as possible. Volatile liquids are dried by long contact with some hygroscopic solid like calcined potassium carbonate, anhydrous copper sulfate, quicklime, baryta, or other dehydrating agent that has no chemical action on the liquid; gases, by passing through a column of anhydrous calcium chloride or phosphoric acid.

B. Substances altered at temperatures above the ordinary are dried in a "desiccator" surrounded by an atmosphere which acts as a conveyor of the moisture of the substance to a hygroscopic material.

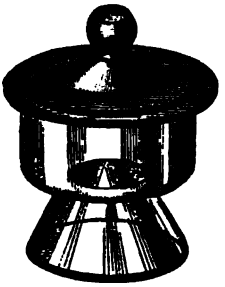


Fig. 12. $^1/_4$-$^1/_6$

The desiccator or exsiccator, Fig. 12, is a heavy glass cup with a cover fitted by a ground joint. A sheet metal shelf perforated with various sized holes rests on a flange near the middle of the cup, or a wire triangle is supported on legs encased in glass tubes to protect the wire from corrosion by the exsiccant. The shelf or triangle carries different sized crucibles or dishes holding the substance to be dried. In the bottom of the desiccator is a layer of fused calcium chloride or sand saturated with concentrated sulfuric acid, the latter drying the air to a greater degree than the former.* The time required for drying a substance (at least several hours) may be considerably shortened by rarifying the inclosed air by exhaustion through a tube projecting from the desiccator or its cover.

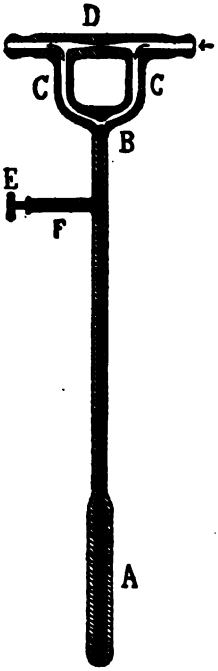


Fig. 14. $^1/_4$

A modification of the above is by Hempel. The edge of the cover is curled inwardly forming an annular cup also filled with the exsiccant, thus providing a drying medium both above and below the substance. Another form, not so portable, is a shallow porcelain dish with several radial ribs to support dishes containing the material to be dried or preserved from moisture. The dish is partly filled with concentrated sulfuric acid and stands on a ground-glass plate and covered by a large bell-jar.

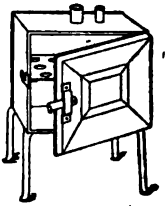


Fig. 13.

For substances decomposed by sunlight, desiccators are made of yellow glass to exclude actinic rays.

C. A number of organic bodies, though partially decomposed at 100° may safely be dried at a temperature somewhat below this and much more rapidly than in a desiccator.

The air-bath, Fig. 13, is a box of sheet copper with riveted joints, supported over a Bunsen burner by four detachable legs, and the front a door hinged at the side. A thermometer passes through a cork inserted in a ring at the top of the box, the bulb situated near the center of the bath. The containing vessels are supported on a tin-plate shelf about half-way up, since the bottom of the bath is at a higher temperature than is shown by the thermometer.

The flame of the burner may be adjusted to give any

* Chem. News, 1891—1—151.

degree of heat up to 300° — higher than this is destructive to the bottom plate. To maintain a uniform temperature, many form of regulators or thermostats have been devised, to control the flow of gas to the burner independent of any irregularity in the gas-pressure. One is shown in Fig. 14; the glass bulb A filled with mercury hangs in the bath, and whenever the desired temperature is slightly exceeded the mercury expands and rises so far as to partly close an aperture B in the tube C through which the gas flows to the burner, diminishing the size of the flame. A screw E presses against the mercury in the branch tube F and provides for adjusting the height of the mercury column to maintain any given temperature. Cooling of the bath below the proper temperature is immediately followed by an increased flame. Since a sudden increase in the volume or pressure of the gas admitted to the burner would result in an abrupt closing of the orifice and extinguish the light, a small hole at D allows just enough gas to pass to keep it alight or feed a small pilot-light.*

Through a large glass tube passing horizontally through the oven and projecting several inches at each end may be passed a current of some neutral gas, the tube holding boats containing bodies affected by the oxygen of the air.†

Venable ‡ describes a drying apparatus constructed of a glass bell-jar set on a sand-bath or a ring of asbestos board resting on an iron plate. The bell-jar has three mouths, one holding a thermometer, the other two for entrance of air and egress of aqueous vapor. An electrically heated oven is described by Richards.§

D. Most oxides, minerals, anhydrous salts and the like are heated to the temperature of boiling water; usually an exposure for an hour is sufficient to remove all moisture from a fine powder.

The water oven has the advantage over the air bath of maintaining nearly the temperature of 100° without attention or special appliances. It is of the same construction with the exception that the top, bottom and three sides are double. The space between the walls is partly filled with water kept boiling by a Bunsen burner. The temperature of the interior approximates 100° as nearly as is necessary for most purposes.

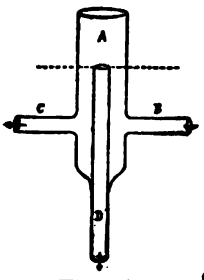


Fig. 15.

As the water evaporates through an opening at the top it must be replenished from time to time unless the oven is provided with an appliance to refill it automatically, such as the one shown in Fig. 15. A continuous stream of water enters the cup A from B and flows to the oven through C; the height of the upper orifice of an overflow pipe D determining the water-level in A and consequently in the oven. Or if the opening into the water chamber is closed with a cork carrying a vertical open glass tube many feet long, the arising steam will be largely condensed by the air and returned.

A hygroscopic solid or semi-solid is best dried in a broad, light glass bottle with ground stopper. After cooling, the stopper, inserted while the bottle is still hot, is apt to stick fast from rarefaction of the air, and Mason proposes to provide it with a stopcock that may be opened to admit air to the bottle.

Viscous bodies are more quickly and thoroughly dried if previously admixed with an equal weight of sand or other anhydrous powder. In some cases there is an additional advantage in that the residue is left in a pellicular form easily permeated by solvents.

* Chem. News, 1890—1—4 and 24.
† Journ. Socy. Chem. Ind., 1896—417.
‡ Journ. Amer. Chem. Socy. 1898—272.
§ Amer. Chem. Journ. 1899—45.

When a constituent other than water is lost on drying it may be retained by the addition of some reagent that will combine with it, as anhydrous oxalic acid for ammonia, or an alkali carbonate for a volatile acid. Or the vapors may be passed through an absorbent to retain the volatile constituent.

For a direct determination of moisture the drying is done in a glass tube one end connected with a reservoir of dry air, the other with weighed bulbs filled with dried calcium chloride or other desiccator. If the amount of water is considerable, the substance is placed in a small flask connected with a graduated tube; the combination is exhausted by a vacuum pump, the tube cooled in a freezing mixture, and the flask gently heated. The moisture distills into the tube where its volume can be measured or the water weighed.

E. A comparatively few bodies must be dried at temperatures above 100° for specific reasons.

When it is desired to maintain an even temperature somewhat above 100°, a small oven may contain between the walls an organic liquid, of a suitable boiling point. Thus, toluol boils at 107°, xylol at 136°, anisol at 150°, pinene at 160°, anilin at 180°, naphthalin at 200°, and diphenylamine at 310°. An aqueous solution of calcium chloride boils at from 101° to 178° according to concentration; to prevent the solution from becoming more concentrated by evaporation of the water, an inverted condenser is held in a cork closing the hole at the top, to condense and return the steam. Usually, however, the drying is done in the air-bath.

For the very hygroscopic manganese ores (superoxides), Fresenius advises a thick iron plate with a number of cup-shaped depressions arranged in a circle near its periphery, into each of which fits a metal dish. The Bunsen burner flame is under the center of the plate, and one of the dishes is filled with iron filings surrounding the bulb of a thermometer showing its temperature and consequently that of the ores in the other dishes.

Liquids unaltered at 100° may be dried at this temperature, but it is safer to employ one considerably higher, as for physical reasons all the water may not be driven off at its boiling point; this phenomenon may be noticed with the oils and fats, and many precipitates are said to be subject to it. Yet it must not be forgotten that many apparently stable bodies are somewhat volatile or are decomposed even at 100° and one must be cautious in this respect. A good plan is to finish by moistening the substance with absolute alcohol and evaporating at a moderate temperature.

For soaps, wood fiber and the like it is recommended to heat a suitable quantity of paraffin oil to 250°, cool and weigh. The weighed sample is introduced, the oil heated to 240°, and reweighed. All the moisture is said to be expelled without decomposition of the substance.

In drying above 300°, a considerable variation in temperature is seldom of consequence, and the heat may be applied by a sand or metal-bath (a shallow iron dish filled with sand or an easily-fusible alloy), or by a direct flame as is most convenient.

CHAPTER 3.

THE BALANCE AND WEIGHTS.

Practically our only means of measuring mass is by weight, and since the correctness of every analysis, with scarcely an exception, depends primarily on this operation, it is evident that the balance used should be of the highest attainable precision. The obvious importance of this subject calls for a somewhat extended discussion of the principles of its construction and rules for its employment.

As at present built by a number of European and American manufacturers, the analytical balance is always of one form differing only in details. The emulation between them has resulted in establishing a high standard, and one may now rely on receiving a first-class instrument when purchasing of a reputable firm, and at a price quite reasonable considering the care and skill bestowed on its manufacture, and the patience in its adjustment. The few variations of construction and fittings are of minor importance and need be given little consideration — a belief in the intrinsic superiority of the productions of any one maker is often only the reflection of a personal preference born of familiarity with their manipulation and behavior.

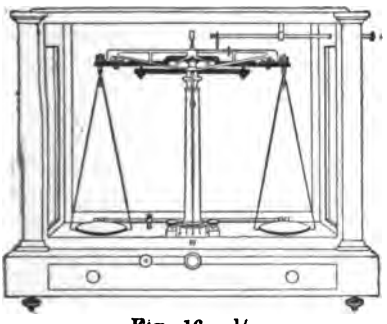
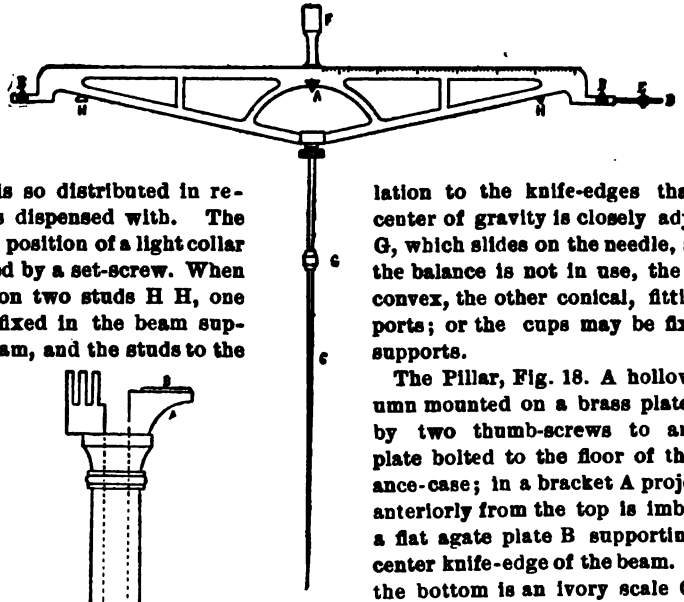


Fig. 16. $^1/_{10}$

Brief. The analytical balance is essentially a light metal beam oscillating on frictionless bearing located exactly in the middle, and having a pan suspended from a similar bearing near each extremity, with an arrangement to support the beam and pans when the balance is not in actual service; all being inclosed in a glass case. The parts of a modern balance, Fig. 16, of the style originated and perfected by American builders may be described as follows: —

The beam, Fig. 17. This was formerly made of some light wood, but at present of brass, bronze or hardened aluminum, lacquered, to prevent corrosion by acid fumes. The form is a truss or hollow triangle braced at intervals by cross-bars, thus uniting the important qualities of rigidity and lightness. Across the center is fixed a triangular knife-edge, A, either of hard steel, agate or carnelian set in metal, or iridosmine. The ends of the beam are each provided with a similar knife-edge B, B, standing in the reverse position, the edge being upward; the three are firmly clasped in the beam and correctly located once for all by the maker. A vertical needle C, about as long as the beam, depends from its center to exhibit the angle of its deviation from the horizontal, and from one or both ends extends a threaded wire D, carrying a nut E, that may be screwed in or out to restore the equilibrium if disturbed from any cause. In the older balances equilibrium was obtained by altering the angular position of a light vane, a short metal strip centered at the bottom of the post F, sometimes terminated by a threaded wire carrying a nut.

The center of gravity of the balance is brought up to the proper height by a post F, rising from the center of the beam; in some balances the weight of the



beam is so distributed in relation to the knife-edges that the center of gravity is closely adjusted by the position of a light collar G, which slides on the needle, and is secured by a set-screw. When the balance is not in use, the beam rests on two studs H H, one convex, the other conical, fitting in cups fixed in the beam supports; or the cups may be fixed to the beam, and the studs to the supports.

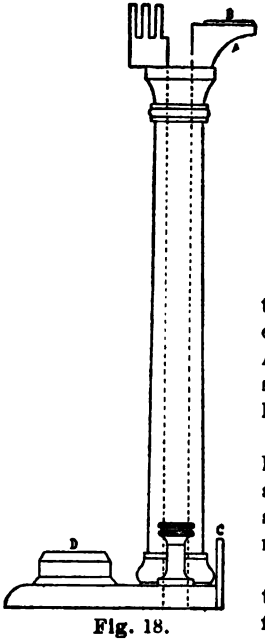


Fig. 17.

Fig. 18.

The Pillar, Fig. 18. A hollow column mounted on a brass plate held by two thumb-screws to another plate bolted to the floor of the balance-case; in a bracket A projecting anteriorly from the top is imbedded a flat agate plate B supporting the center knife-edge of the beam. Near the bottom is an ivory scale C traversed by the needle, an arc divided right and left from the middle zero; the balance is usually adjusted so that a space of five divisions corresponds to a weight of one milligram. A reading glass of medium refraction in front of the scale is an agreeable addition especially in an illy-lighted balance room.

Fixed to the pillar at the rear is a circular spirit-level D, or two tubular levels at right angles, showing any deviation of the pillar from the vertical, and consequently of the beam from the horizontal when the needle points to zero.

The Stirrups, Fig. 19, are two hollow rectangles of thin sheet German silver, the top bar A inclosing the flat agate plate B which rests on the end knife-edge. The projecting ends of the bar have edges C C beneath caught by the V's of the beam-supports. Below is a double hook D, the upper recess for the suspension wires of the scale-pan, the lower for hanging U-tubes, etc., to be weighed.

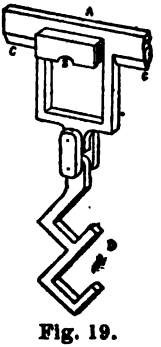


Fig. 19.

The Scale-pans are circles of light sheet metal stiffened by a down-turned rim and hung from the stirrup hooks by bent wires. The length of the wires is immaterial (assuming that there is no friction between the end knife-edges and their bearings) but it is essential that the pans be suspended in such a manner that they may swing freely at right angles to the beam, so that if an object be placed on the pan away from its center, the pan will shift in the opposite

direction so far that the center of gravity will lie vertically below the middle of the knife-edge, which will consequently sustain the load uniformly throughout its length, Fig 20. This is provided for by the flexible joints in the stirrups.

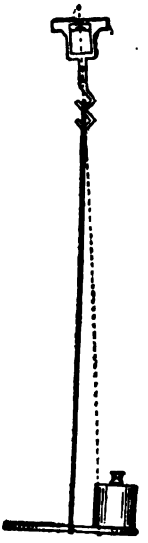


Fig. 20.

Beam Supports. It being indispensable for preserving intact the keenness of the knife-edges that they press upon the agate planes only when the balance is in actual use, a system of supports, Fig. 21, carries the beam and stirrups. It consists of a reeded wheel, A, fitting on the anterior end of a horizontal shaft B extending back to the center of the balance case; immediately under the pillar is keyed a cam, cardiod, or eccentric C, on the periphery of which rests the lower end of a rod D sliding up and down within the pillar. On the upper end of the rod is a cross-head E. Through this pass two screws, F F, held in position by jam-nuts; on their points rest the two arms, G G, working on a central pivot H. Near the end of each arm is a small stud, II, receiving the cup beneath the beam, and also a bifurcated extension J with a pair of V-shaped grooves catching the upper bar of the stirrup, Fig. 21A.

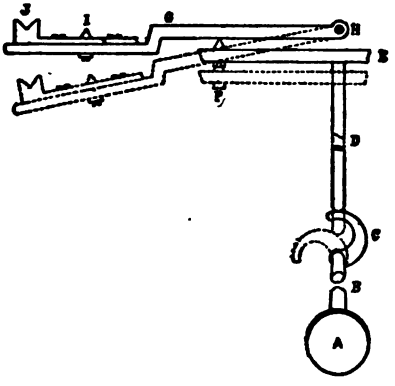


Fig. 21.

As the cam is rotated by turning the wheel, the rod and crosshead drops, lowering the arms GG to the position shown by the dotted lines. It will be noticed that when the wheel is turned at a uniform speed the rapidity of the motion of the rod and arms is not correspondingly uniform, the variation due to the eccentricity of the cam; the upward motion is continuously retarded, so that the impact of the supports with the beam and stirrups is free from shock provided the wheel is turned with reasonable slowness.

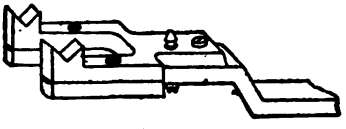


Fig. 21A.

The whole arrangement demands the most careful construction to insure that the beam and stirrups shall invariably be lowered to the same position and the beam raised from an inclination without any sliding of the knife-edges along or across the planes.

For rigidity, the inner ends of the arms GG are broadened and dove-tailed, the firm hinge-joint, Fig. 22, preventing any lateral motion of their extremities; the axis of the pivot is located exactly in the line of junction of the center knife-edge that the arcs described by the cups II and the studs HH (Fig. 17) shall coincide; and (unless the stirrups do not engage with their supports until after the beam is brought to a horizontal position) the edges CC (Fig 19) of the stirrups are situated in the plane of the inclosed agate plates BB. Adjusting screws are provided to compensate for any wear or derangement.

Fig. 22.

Pan-supports. The pans rest on the plush covered tips of a pair of light fingers A, Fig. 23, which are pivoted at B., and the posterior ends fixed to the extremities of a shaft C running across the rear of the balance case. Near the middle of C depends an arm D, the lower end hooked to a rod E moving longitudinally and terminating in a button F to the left of the wheel. A light spiral spring encircles E forcing it and the arm D forward, thereby depressing C and raising A. When the button is pressed the reverse takes place, and the pans are set free. The tension of the spring is regulated by turning the button, and equality in height of A and A′, by the screw H. On the rod E near the button is a transverse groove, into which drops a catch when the button is pressed in, keeping the fingers AA′ down until the catch is released by pressing a wire near the button. A better arrangement provides for holding down the fingers when the button is rotated through a small arc.

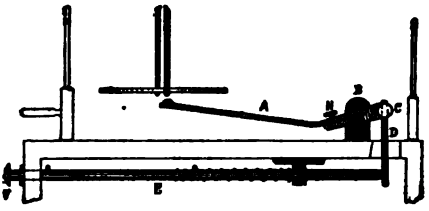


Fig. 23.

The tips of the pan-supports should press against the exact centers of the pans to prevent deflection of the stirrups. In a late improvement the tips are conical in form and rise into corresponding cavities beneath the pans thereby insuring an exact centering of the latter when their swinging is arrested.

The Rider-arm. This is a brass rod hung horizontally above and behind the beam. It extends from the middle to the exterior of the balance case, terminating in a knurl by which it can be rotated or moved longitudinally. Across the inner end is an adjustable hooked wire A, Fig. 24, which catches the loop of a bent wire weight B called a "rider." By manipulating the rider-arm the rider may be hung at any point on the right-hand half of the beam, or suspended above it.

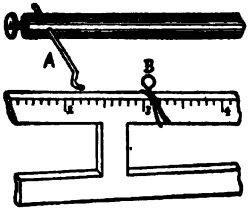


Fig. 24.

The Balance Case. A frame of well-seasoned wood or metal, glazed on the sides and top, is mounted on leveling screws and incloses the entire mechanism for protection from dust, drafts and acid fumes. The front and back panes slide upward, the former counterpoised by sash-weights; both may be locked by the wheel. The floor may be of wood, plate-glass or black marble, preferably the last named, as wood is apt to warp and glass to crack.

Special Balances. To save time in transferring weights to and from the pans, balances have been designed where any weights of a set may be placed on the pan or removed while the case is closed, by manipulating the corresponding key of a key-board situated in front of the case.

Bunge, Hase, and others have devised attachments to show at once the weight of an object to within a centigram. The object to be weighed being in the left-hand pan, a spring or bent lever is brought in contact with the beam, and on releasing the supports, a pointer actuated by the spring or lever shows the approximate weight on a scale graduated in grams and fractions. The apparatus is then thrown out of contact with the beam, and the exact weight found in the usual way. In the plan of Serrier,* one end of a long chain is attached to the balance beam, the other end to a lever supported by the balance case. As the lever is raised or lowered a correspondingly shorter or longer part of the chain hangs from the beam. The height of the lever is read on a scale.

In Taylor's apparatus a long thread made of glass or celluloid is firmly held horizontally at one end, and to the other is suspended a pan carrying a pointer traversing an

* Analyst, 1897—196.

arbitrary scale; the sample is filled into the pan until the pointer sinks to the division previously indicated when a standard weight was in the pan. It is specially adapted for weighing a number of equal quantities of metal drillings, and for this purpose the drillings as they are cut from the metal bar may fall directly into the pan.

Phillips† proposes for similar purposes an instrument in the shape of a hydrometer, the bulb being a gilded brass ball and the stem an aluminum tube. Across the top of the stem is fixed a horizontal bar, the ends perforated to slide up and down on two rods attached to the hydrometer jar. On the cross-piece is fastened a small scale-pan, and below it a pointer. Another pointer extends from a collar that slides on one of the uprights and may be fixed at any point by a set-screw. The jar being filled with water, an analytical weight of the proper denomination is placed in the scale-pan and when the instrument has come to rest, the pointers are made to coincide. The weight is then removed and the sample dropped in the pan until the pointers again coincide. The range of weight is necessarily small and the delicacy depends on the diameter of the stem, e. g., one of a diameter of 1-16 inch sunk a depth of 3 7-8 inches, with a weight of .2 gram.

The elasticity of a delicate coiled spring is applied in the well known Jolly's balance, designed particularly for taking the specific gravity of minerals.

Attempts have been made to provide a substitute for the easily dulled knife-edges, such as hemispheres rolling on the plates, etc., though none of them have come into extended use for analytical work. In the 'torsion balance' the beam grips the middle of a taut horizontal wire held firmly at the ends by two supports; the ends of the beam hold similar wires terminating in the upright bars of the stirrups. As the beam is inclined the wires are twisted, the moment of their torsion being for small angles proportional to the load. A "dynamic balance" has been proposed on the principle that a load applied above the fulcrum of a compound pendulum raises the center of gravity and correspondingly alters the rate of vibration.

A comparison with another style of balance of German manufacture shows several points of difference from the one just described. The case has three doors, and is without a drawer for weights, etc. The beam is much wider, and inverted, the obtuse angle being above, and its center is subtended by a vertical threaded wire carrying a nut which may be screwed up or down to adjust the center of gravity. To the front of the lower bar of the beam and parallel with it is fixed a strip of ivory whose upper edge carries the rider and is in a horizontal plane with the line joining the knife-edges. The beam supports are not pivoted but firmly attached to the cross-head and move vertically; and the pan-supports have a positive motion, generated by a second cam on the shaft so adjusted as to raise them slightly in advance of the beam-supports in order that the latter engage with the beam only when it is in a horizontal position. The spirit-level is replaced by a plumb bob hanging at the rear of the pillar, and the joints in the stirrups by a second knife-edge below and at right angles to the first.

Short-beam Balances. There has been a tendency of late years to considerably shorten the beam, reducing it from 10 or 12 to 6 or 7 inches, thereby giving a more rapid movement to the needle. The sensibility of the balance is theoretically decreased, as the beam may be considered as a lever of the first class, but it is claimed that this is offset by the greater stiffness and lightness of the shorter beam. While there is a diversity of opinion as to whether the operation of weighing is really expedited to any great extent, certainly they have met with favor and are supplanting the older form.

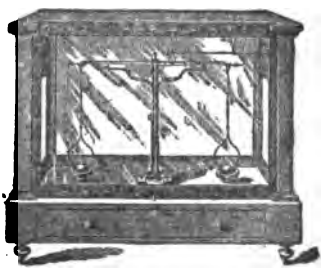


Fig. 25.

The Assay Balance, Fig. 25, for weighing silver buttons and gold from the fire-assay is far lighter and more delicate in construction, as it

† Chem. News, 1895 — 216.

is designed for a load not exceeding a gram; one one-hundredth of a milligram is shown on one of the finer grades. A noticeable difference is the design of the beam supports as well as the end knife-edges and the agate plates.

Fig. 26.

As shown in the figure no supports are provided for the stirrups. The end agate bearings are kept in position on the knife-edges by a semicircular furrow cut in the former terminated by thin metal plates; friction between these and the ends of the knife-edges is prevented by cutting the latter at an angle, Fig. 26. In the more precise instruments a system of supports similar to that of the analytical balance is provided.

An equation expressing the sensibility of the balance may be deduced as follows: —

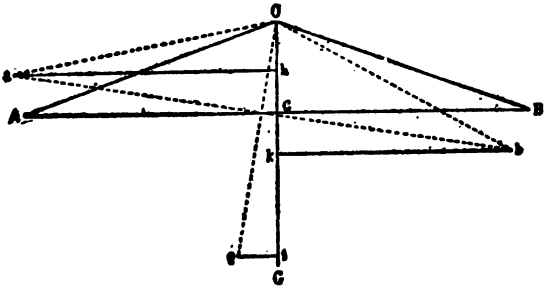


Fig. 27.

In Fig. 27 let A and B be the end knife-edges, and A B a line joining them; O G a line perpendicular to A B with the point of intersection at G; O, the center of oscillation, and G, the center of gravity of the beam. Let M be the weight of the beam; P, a weight in the pan supported by A; and P′, an equal weight in the pan under B. The line A B being horizontal we have by the law of levers,

$$P \times A\,G = P' \times B\,G \ldots\ldots (1),$$

If now a small weight p be dropped into the right-hand pan the beam will incline, finally coming to rest in the position a O b while O G moves to O g. Obviously the greater the angle g O G produced by p, the more sensitive the balance.

Draw the perpendicular a h, b k, and g i, and call the angle $A\,O\,a = B\,O\,b = G\,O\,g = \theta$, and $A\,O\,G = B\,O\,G = \alpha$. Since the balance is now in equilibrium at a O b, we have p balanced by $M \times g\,i$, and therefore

$$P \times a\,h + M \times g\,i = (P' + p) \times b\,k \ldots\ldots (2).$$

the "equation of equilibrium."

$$\text{Now } g\,i = O\,g \sin\theta = O\,G \sin\theta \ldots\ldots (3).$$

Also $a\,h = a\,O \sin(A\,O\,a + A\,O\,G)$.

Or $a\,h = A\,O \sin(\alpha + \theta)$ since $a\,O = A\,O$.

And (according to the well-known theorem, $\sin(x + y) = \sin x \cos y + \sin y \cos x$),

$$a\,h = A\,O \sin\alpha \cos\theta + A\,O \sin\theta \cos\alpha,$$

and since $A\,O \sin\alpha = A\,G$, and $A\,O \cos\alpha = O\,G$, then

$$a\,h = A\,G \cos\theta + O\,G \sin\theta \ldots\ldots (4).$$

In the same manner we find

$$b\,k = A\,G \cos\theta - O\,G \sin\theta \ldots\ldots (5).$$

Substituting the values of (3), (4), and (5) in equation (2),

$P \times A\,G \cos\theta + P \times O\,G \sin\theta + M \times O\,G \sin\theta = (P' + p) \times A\,G \cos\theta - (P' + p) \times O\,G \sin\theta$.

Reducing,

$$\frac{\sin\theta}{\cos\theta} = \frac{(P' + p) \times A\,G - P \times A\,G}{P \times O\,G + M \times O\,G + (P' + p) \times O\,G}$$

or

$$\tan g\ O\ G = \frac{p \times A\ C}{(P + P' + p) \times O\ C + M \times O\ G} \quad \ldots\ldots\ldots\ldots (6)$$

From equation (6) it will be seen that tan g O G — a measure of the deflection of the needle or the inclination of the beam — is the greater,

1. The greater the difference between the weights in the pans (increase in p).
2. The longer the beam (increase in A C).
3. The less the weight of the beam (decrease in M).
4. The nearer the axis of oscillation to the line joining the end knife-edges (decrease in O C).
5. The less the load on the pans (decrease of $P + P' + p$); but if O and C are made to coincide (as they do in all balances), O C becomes zero, $P + P' + p$ vanishes, and the balance is equally sensitive in this respect with every load.
6. The less the distance between the line joining the end knife-edges and the center of gravity of the beam (decrease of O G). If, however, O and G as well as O and C are made to coincide, the equation becomes

$$\tan g\ O\ G = \frac{p \times A\ C}{\text{zero}} = \infty = \tan 90^\circ,$$

and for every difference in weight in the pans, however small, the needle will tend to assume a horizontal position. And if O C and C G were negative, the needle would describe more than a quadrant.

Details of construction. Several essential features must be given consideration by the builder.

1. The aggregate weight of the beam, pans and hangers should be as small as is consistent with their rigidity, that the inertia of the system may be more easily overcome by a small accession of weight in the pan or on the beam.

2. Considering the balance as a compound pendulum, it is clear that the center of gravity must lie below the bearing line of the center knife-edge and as near to it as is consistent with a reasonable rapidity of vibration (say 10 to 15 seconds) for if above the line, the beam will be in unstable equilibrium — top-heavy; if exactly in the line, in neutral equilibrium and refuse to vibrate; and in proportion to its distance below will a greater weight be needed to incline the beam, for the lower the center of gravity is situated from the fulcrum — that is, away from the position of maximum sensitiveness — the more stable will be the equilibrium. And clearly, any increase of weight applied to the end knife-edges (i. e. on the pans) will tend to raise the center of gravity nearer the axis of the center knife-edge; the gain in sensibility, however, is neutralized in a great measure by the inertia and friction engendered.

3. The edges of the three knives must lie in the same plane, as otherwise the center of gravity will shift to an unallowable degree under different loads; for if the center knife-edge is below a line joining the end ones, any increase in weight on the latter will tend to raise the center of gravity, and conversely. For this reason only the slightest flexure of the beam under the maximum load is permissible, and since perfect rigidity cannot be attained without a sacrifice of lightness, the maker endeavors to secure an alignment when the pans are weighted with about one-half of the greatest load the balance is designed to carry.

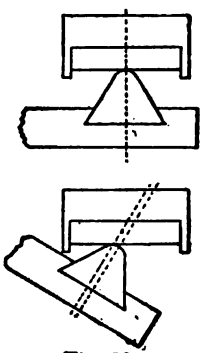


Fig. 28.

Each knife-edge should be horizontal in order that a load may be sustained equally throughout its length, and the three edges be at exact right angles to the axis of the beam — the center edge, in order that the beam at every inclination shall align with its supports, and the end edges, that they remain horizontal when the beam is

inclined. The knives must also be as keen as possible, not only to lessen friction, but also that the distances from one another of their lines of contact with the agate plates shall be identical in every position the beam may assume; the effect of a blunt edge is shown exaggerated in Fig. 28.

The agate plates must be exact planes and highly polished that their contact with the knife-edges shall approach geometric lines. Under a load we may conceive that the junction of the edge of the knife and the plate beneath becomes an arc whose radius increases with the load.

4. Theoretically, the end knife-edges should be exactly equidistant from the center, and a remarkably close approximation is attained by modern builders. The inevitable slight inequality may be counteracted by certain modes of weighing.

5. Good workmanship throughout is to be insisted on when selecting a balance, particularly that the wood of the case shows no signs of warping or cracking; that the rider-arm is so located that the hook will fairly catch and lift the rider without striking the beam; that the needle swings close to the scale without touching it at any point; and that the mechanism of the beam supports and pan arrests, the movement of the rider-arm, and the sliding of the front pane, all work smoothly without undue friction. Finally, it is well to consider that, other things being equal, the less complicated the mechanism and the fewer the movable parts the better. The profusion of adjusting screws and other accessories, a distinguishing feature of the instruments of some manufacturers, are not only practically useless but corrodible and dust-catching, a positive detriment.

Before sending a balance into the market the builder carefully examines it to be convinced that these requirements have been complied with. The equidistance of the knife-edges is tested by transferring equal loads to opposite pans; for their being at right angles to the beam by hanging each pan by a wire hook to the rear extremities of the end knives and weighting one pan until the balance is in equilibrium, then transferring one of the hooks to the anterior end, when the equilibrium should be unaltered; for their collimation by raising the center of gravity until with empty pans, the vibrations are very slow, and observing the rate with the maximum load; and finally lowers the gravity-bob on the needle until the beam swings with the proper velocity. It will be found that the sensibility of a balance can be increased by raising the bob, but this is not as a rule necessary or advisable, as the errors in weighing with a reasonably precise adjustment are usually the least important of those affecting every analysis.

Fig. 29

Care of a balance. The foregoing shows the importance of proper treatment of an instrument of such refinement. Carelessness and neglect will quickly impair its sensitiveness, and once it is in proper working order the less experimenting with the various provisions for adjustment, the better. Such minor corrections as an occasional turn of the nut at the end of the beam may be required, but any further alteration is to be made with caution,

and only competent hands ought attempt the rectification of a serious fault. The balance should be reserved for analytical purposes exclusively, a less delicate scale (as in Fig. 29) serving to weigh out reagents, etc.

It may stand on a heavy table in a place free from vibration of the floor, on a shelf bracketed to a wall, or best on a pillar rising from the ground, and away from draughts and direct sunlight. Where the jar of passing vehicles or trains causes a tremor of the needle, a thick rubber sheet laid under the leveling screws, or inserting them in rubber stoppers, will absorb the vibration partially if not entirely. The room should be well lighted and have a fairly uniform temperature, as sudden changes may cause irregularities by expanding or contracting the beam ununiformly.

The air in the balance case may be kept fairly dry and the steel parts preserved from corrosion by a beaker holding anhydrous calcium chloride or quick lime, or *partly* filled with concentrated sulfuric acid. The case should always be kept closed when the balance is not in actual use, and a baize or enameled cloth bag drawn over it during the night will aid in keeping out dust and fumes. Agate knives advance the original cost of a balance somewhat, but are advisable where the balance room communicates with a laboratory where acid fumes are abundant.

Setting up a balance. As received from the dealer the beam is found fastened to the bottom of the drawer of the balance case. The needle is to be tightly screwed into the beam, taking great care that it is not bent in the operation. The supports are raised and the beam slowly and carefully lowered on them, observing that the needle goes in front of the scale. The stirrups are then slipped over the ends of the beam into the V's of the supports, with the openings of the hooks to the front; the upturned ends of the pan-wires are inserted in the holes beneath the pans, and hung on the upper hooks. All the detachable parts are marked with points or letters to show their contiguity at the time the balance was adjusted by the maker, and this arrangement must be exactly reproduced. The bubble is then brought directly under the ring at the center of the spirit-level by adjusting the leveling screws of the balance case, the rider is hung on the hook of the rider-arm, and the balance is in readiness for examination by the directions on page 41; but no attempt at equilibration is to be made before some hours have elapsed for the beam to assume or return to the temperature of the balance room.

Weighing. Before proceeding to make a weighing, the pans are to be dusted with a camels-hair pencil, and the equilibrium of the balance tested, seeing that the rider is off the beam, and that the balance stands level. The wheel is turned very slowly until the knives rest on their bearings; especially is this important when the supports separate them too far — they should barely part. The wheel is then turned as far as it will go and the button pushed in. Should the needle remain stationary the rider is momentarily dropped on the beam, but the extent of the first vibration should not be so great as to cause the beam to touch its supports, for a slight shifting may take place if their axis does not coincide with the bearing line of the center knife edge.

Nothing is to be placed on the pans or removed while the beam is unsupported, and the pan-rests should bring the needle to zero before the location of the rider is changed or the beam-supports raised. The case should always be closed while taking an exact weight. Any twist or shift of the stirrup while the beam is free is to be avoided, not that the beam length is altered thereby, but because the edges of the knives may be injured, and if the stirrup-case comes in contact with the knife-edge the beam will refuse to vibrate.

Only glassware, crucibles, dishes and the like are set directly on the scale pans, other materials being held in suitable containers. A pair of watch-glasses of exactly equal weight usually accompanies the balance for weighing powders, as well as a light German silver stand, Fig. 30, to support a test-tube containing a liquid. Most powders, crystalline salts, and dried or ignited precipitates acquire moisture from the air so slowly as to need no further protection than covering the dish or crucible containing them, while hygroscopic, efflorescent, or volatile substances are held in a test tube closed by another of equal length and slightly greater diameter, or a weighing-bottle. Paper filters are inclosed between two watch-glasses, bound together by a spring brass clip, Fig. 31.

Fig. 30. $^5/_{12}$

A gas is weighed inclosed in a light glass bulb approximately counterpoised by another of the same size, and as these are too bulky to enter the balance case, they are hung to the stirrups by thin wires passing through the bottom of the case and the shelf on which it rests into a brick-walled cell wherein the temperature is not subject to sudden changes.

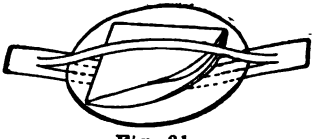


Fig. 31.

Temperature in weighing. After heating a crucible or dish it must be allowed to cool to the temperature of the balance-room before placing on the scale-pan as the air currents arising from a body warmer than the surrounding air tend to raise one pan and depress the other. In especially delicate work the vibrations of the needle are observed through a telescope from a distance of several feet that the radiated heat of the body may not affect the length of the beam or induce air-currents.

It is plain that the more extensive the surface of a body exposed to the air, the greater its capacity for condensing moisture and consequent variation in weight at different times through a change in the hygroscopic condition of the air, and on rainy days it is almost impossible to obtain accordance in several weighings of a bulky object. Hence vessels containing substances for weighing should be as small and compact in form as circumstances will permit, and remain in the balance for fifteen minutes or more before taking their exact weight. It is said that in weighing an open wide-mouth vessel containing a volatile liquid, air currents are set up by evaporation, the more extensive the drier the air of the balance case.

Weighing by reversal and substitution. Besides the ordinary direct mode there are two others which eliminate or correct for an unequal length of the beam arms. In the method of reversal, the object is balanced first on one pan, then on the other; the arithmetical (strictly the geometrical) mean of the two being the true weight. In that of substitution, a counterweight somewhat heavier than the object is weighed; the object is then placed in the pan with the weights, and by the sum of such of these as must be removed to restore the equipoise, the true weight of the object is given. And in weighing in the usual manner it should be the rule to reserve the right-hand pan for the weights only.

Weighing by vibrations. Theoretically, equality in weight is shown by a journey of the needle the same number of divisions to each side of the zero, also when the needle remains at zero after the supports are disengaged. The former indication is to be preferred since the accession of a weight inadequate

to move the needle from a state of rest will perceptibly shift the arc of its vibration. But as the excursions continually lessen in amplitude, uniformly in theory, but more or less irregularly in practice, several consecutive readings on each side are averaged in preference to accepting a single swing.

With the load in one pan slightly the heavier and a representing the number of divisions swung to one side and a' to the other, then $\frac{1}{2}(a - a')$ locates the secondary point of rest, and if the displacement corresponding to an overweight of one milligram is determined for different loads, in practice fractions of this weight may be quickly and quite accurately estimated by the eye.

Weighing in vacuo. A correction is made in the most refined analyses for the buoyancy of the air which diminishes the true weight to the extent of the weight of a volume of air equal to the volume of the object weighed.* The latter may be taken as the product of its apparent weight by the reciprocal of its specific gravity, and the average weight of one cubic centimeter of air as .0012 gram.

When an object has the same specific gravity and consequently an equal volume with the sum of the weights balancing it, both are equally lightened, and the apparent is also the true weight. But when the object has a lower specific gravity and greater bulk, its apparent weight must be increased by the weight of a volume of air equal to the difference between the volume of the object and that of the weights, and conversely. Assuming the weights to have been standardized in vacuo, if G represents the specific gravity of the object; G', that of the weights; and W, the weight of the object; then

$$\text{Weight in vacuo} = W\left[1 + .0012\left(\frac{1}{G} - \frac{1}{G'}\right)\right] \text{ grams.}$$

Thus, a platinum wire sp. gr. 21, balancing a one-gram weight sp. gr. 8.5 weighs in a vacuum, .999916 gram.

In analysis the error for solids and liquids is unimportant in ordinary work as it affects both the weight of the substance taken for analysis and those of the separated constituents, one largely compensating the other. For gases it cannot be neglected, so for simplicity the glass globe inclosing one is nearly counter-balanced by another of the same size and slightly less in weight.

A new balance of the best quality suitable for general analytical work:—

Should carry up to 100 grams in each pan.

A weight of one milligram should alter the point of rest of the needle at least 4 mm., and the sensibility be not greatly decreased with the maximum load.

On reversing a load of one gram in each pan, a difference of not more than .0003 gram should be found.

Several consecutive weighings of the same object should not differ by more than .0002 gram.

Not more than 15 seconds should be required for one vibration of the needle, and they should slowly diminish in amplitude.

For general work the balance need only show plainly a change of one-half a milligram in the load.

THE WEIGHTS.

The metric system of weights and measures is now almost universally employed in analysis. Although the standard grams of different makers may vary a trifle from the normal gram and from each other, yet this is not a matter of much moment, since the analyst concerns himself almost exclusively with relative rather than actual mass. But it is of the highest importance that in any one set each weight shall be as nearly as possible an exact multiple or factor of every other weight, and it is indispensable that the extent of the

* Chem. News, 1895—1—4.

variation be known to the operator if it be measurable by the means at his disposal, for the delicacy of a balance counts for nothing if the weights are not correspondingly accurate.

Denominations—The Rider. A set (Fig. 32), containing two twenty-gram pieces running down to one milligram is ample for most work. The gram and its multiples are usually of brass, lacquered, gilded or platinized. They are

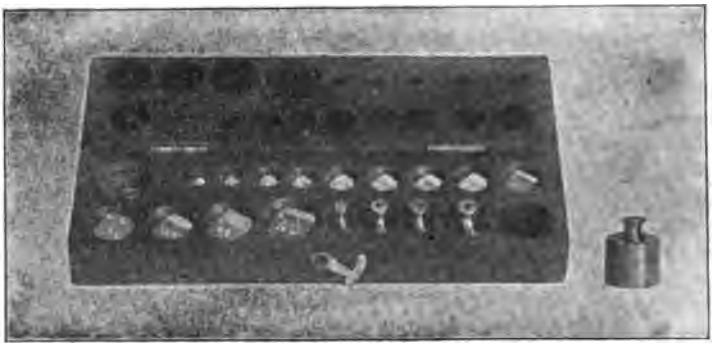


Fig. 32.

cylindrical in form, capped by a stem for handling. By some manufacturers each weight is made a trifle light originally, the stem screwing into the cylinder seals a cavity containing shot and strips of foil to bring up the weight to standard.

A number of materials are in use or have been proposed for analytical weights, but none are free from some objectionable features.* Lacquered brass can be fashioned and adjusted at a moderate cost, but the weights are quickly attacked by acid fumes of the laboratory, the lacquer is hygroscopic, and it is said that the internal blowholes formed in casting the brass are liable to become oxidized and increase the weight of the piece. Gilded and platinized brass weights resist acid fumes, yet the platings are so soft and heavy that slight wear perceptibly reduces the weight of the piece. Quartz and hard glass are incorrodible, though expensive to make, brittle, and liable to become electrically charged. Iridio-platinum is undoubtedly the best material, but for ordinary use the cost of a set of weights is almost prohibitive.

The denominations below one gram are squares of platinum or aluminum foil with an edge or corner bent up to be grasped by the forceps. Fractions of the milligram are made of aluminum wire, but they are so minute and difficult to handle that a substitute is provided in this way: the front of the top bar of the balance beam is divided from the center to the right-end knife-edge into 60, 100, or 120 equal parts, and a bent aluminum wire, Fig. 33, called a "rider" weighing respectively 6, 10, or 12 milligrams, may be hung at will over any division by means of the rider-arm of the balance. Each division therefore corresponds to a weight of one-tenth of a milligram, and the set of weights need have no lower denomination than ten milligrams, or five when the beam has only 60 divisions. In some balances this arrangement is duplicated on the left-hand side.

Fig. 33. 1/1

* Chem. News, 1888—2—197.

Assay weights. For gold and silver ores it is the custom with assayers to report their results as so many ounces (or the money value thereof), in one ton of ore, and a special system of weights has been devised by Chandler to dispense with the tedious calculation from the metric system employed in the assay. The basis is an "assay ton" of 29.167 grams; this weight of ore being taken for an assay, each milligram of gold or silver recovered represents one Troy ounce per ton of 2000 Avoirdupois lbs. In some mints for assaying alloys, the weight of .500 gram is taken as 1000, and the set contains decimals of this down to .0001.

Ivory-tipped forceps are best for handling weights, never the fingers or sharp pointed forceps. The box should be kept closed when the weights are not in use to exclude dust and corrosive fumes. Warping of the box may distort the holes and cause the brass weights to bind, when the holes should be enlarged by scraping with a knife-blade, not with sand or emery-paper as abrasive particles may be left imbedded in the wood.

Experience will show a gain in time by trying the weights in a methodical way rather than at random; beginning with the one judged to be nearest the weight of the object, finding two between which the true weight lies, and gradually narrowing the limits. Thus for a crucible of 15.752 grams the sequence will be about as follows: 20, 10, 15, 17, 16, 15.500, 15.700, 15.800, 15.750, 15.770, 15.760, and by the rider, 15.752. Some of the latter trials may be omitted when the retarded vibrations of the needle indicate an approximation to equilibrium.

Precision of weights. A set is tested by trying each against the corresponding one of a set of known integrity if at hand, or by choosing one piece as a standard and finding the relative weights of the others, comparing each with the sum of such lesser ones as nominally equals it, and those of the same denomination with each other. A new set, professedly of the best quality, should be rejected if a discrepancy exceeding .0002 gram be found in the denominations below the five-gram piece. Above this they need not agree so closely, being generally used merely as counterpoises for crucibles, etc., where their actual weight is a matter of no consequence. Where a greater variance is the result of corrosion or wear of an old set, or with an inferior quality, a table of corrections must be drawn up and applied to every weighing; this plan will be found more feasible than an attempt to adjust the weights themselves. The testing should be repeated from time to time, especially if they are in continuous use.

TESTING THE BALANCE.

Raise the front and back panes of the case, after unscrewing the locking-bolt of the latter with the wheel, and dust the entire mechanism with a camel's hair brush.

Notice that the stirrups and pan-wires are arranged in conformity with the marks thereon, and that the pan-rests touch the bottom of the pans when the beam-supports are raised. Turn the screws under the case until the bubble rests at the center of the spirit-level.

Hang the rider on the hook of the rider-arm, close the balance case and slowly turn the wheel as far as it will go. If the needle does not now point to zero, raise the beam-supports, and adjust the pan-rests by the screw H, Fig. 23.

Lower the beam-supports, push in the button and start the beam to swinging by momentarily dropping the rider on it; but at the first vibration the beam should not come in contact with its supports.

If from a derangement of the position of the center of gravity the beam refuses to swing or oversets, or the time of one vibration exceeds 15 seconds, the collar on the needle should be lowered; but raised if the vibration occurs in less than 8 seconds. Should the arcs traversed to each side of the zero be not equal or nearly so, raise the beam supports and turn the nut on the wire at the end of the beam; allow a few minutes for cooling, and test as before: repeat this until the difference is not over one scale-division.

Again start the beam to oscillating and when the excursions have shortened to about six divisions on each side, begin to record them, marking the swings to the right-hand R, and to the left-hand, L. If the bearings were frictionless and the balance in vacuo the point equidistant from the extremes of the first journey, say L 6.9 to R 6.5 divisions would be the position (0′) at which the needle would eventually come to rest — that is at $\frac{1}{2}(6.9-6.5)=.20$ division to the left of the zero of the scale. To reduce errors of observation and to compensate for the somewhat irregular shortening of consecutive swings, the average of the means of an even number of vibrations is taken as 0′: thus,

Left-hand No load	Right-hand No load	0′ division from 0. Left of 0,	Right of 0.
6.9	6.5	.20	
6.3	6.5		.10
6.3	6.0	.15	
5.8	6.0		.10
5.8	5.5	.15	
5.3	5.5		.10
5.3	5.1	.10	
4.8	5.1		.15

Mean position of 0′, .08 division to the left of 0.

Now place a one or one-half milligram weight in one pan and note the oscillations as before.

Left No load.	Right .5 mmg.	Point of rest, 0″.		
6.0	1.4	2.30 divisions to left of 0.		
5.7	1.4	2.15	"	right "
5.7	1.1	2.30	"	left "
5.4	1.1	2.15	"	right "
5.4	.8	2.30	"	left "
5.0	.8	2.10	"	right "
5.0	.6	2.20	"	left "
4.7	.6	2.05	"	right "

Mean position of 0″, 2.19 divisions to the left of 0.

Subtracting 0′ (.08) from 0″ (2.19) gives the net variation for .5 mmg. of 2.11 divisions from the zero of the scale; therefore one mmg. moves the zero to $2 \times 2.11 = 4.22$ divisions to the left, and one division on the scale with empty pans shows $.001 \div 4.22 = .00023$ gram; assuming that, for small angles, the weight is proportional to the angular displacement of the needle.

The above examination is repeated with loads of say 15, 25 and 50 grams, when somewhat different results will be obtained; for example, a balance of American manufacture:—

Length of beam between the end knife-edges,	256 mm.
Length of needle from center knife-edge,	250 mm.
Length of center knife-edge,	20 mm.
Length of end knife-edges,	10 mm.
Weight of beam, stirrups and pans,	110 grams.
A space of 10 divisions on the scale equals	15 mm.

Weight on each pan.	Deviation for one mmg.	One scale-division equals.	Time of vibration.
No load.	4.22 divisions.	.00023 gram.	15 seconds.
15 grams.	4.08 "	.00024 "	17 "
25 "	4.00 "	.00025 "	18 "
50 "	3.48 "	.00029 "	20 "

Length of arms. The relative distances of the end knife-edges from the center are found from the law of levers — the equality of the products of the length of each arm times its load.

Let L be the length of the left arm, and R, that of the right; A, the load in the left-hand pan, and B, that in the right; and a, a small weight added to A (or shown by needle vibrations) needed to produce equilibrium. Then,

$$L \times (A + a) = R \times B \quad \ldots\ldots (1)$$

If the arms are exactly equal in length, on reversing the loads,

$$L \times B = R \times (A + a) \quad \ldots\ldots (2)$$

But if say the right arm be longer, then a lesser weight b replaces a, and

$$L \times B = R \times (A + b) \quad \ldots\ldots (3)$$

Multiplying (1) and (3) together and reducing,

$$R : L :: \sqrt{\frac{A+a}{A+b}} : 1.$$

Since a and b are very small as compared with A and B, this may be expressed,

$$R : L :: 1 + \frac{a-b}{2A} : 1.$$

Example. $A = 50$ grams; $B = 20 + 10 + 10 + 5 + 2 + 2 + 1$ grams. Left pan $A + .0008 = B$, right pan. Reversing, $B = A + .0003$.

Hence $a = .0008$ gram, and $b = .0003$ gram; and

$R : L :: 1 + \frac{.0008 - .0003}{2 \times 50} : 1$; that is, the length of the right-hand arm is 1.000005 times that of the left.

Variation on repeated weighings. A metal object weighing 50 to 100 grams is counterbalanced by weights and the rider so that the needle swings an equal number of divisions on each side of the zero. The beam-supports are then raised and lowered ten times in succession; a variation of more than one-tenth of a milligram indicates faulty workmanship or maladjustment of the beam supports.*

TESTING THE WEIGHTS.

Before testing the relative correctness of the weights each should be carefully cleaned by brushing or wiping with chamois. Those below the denomination of the gram are made of platinum foil *generally* down to .050 gram, below that of aluminum. The former may be cleaned by heating to redness for a moment in the flame of a Bunsen burner, but aluminum will not admit of this operation.

Assuming the set to contain two twenty-gram pieces down to one milligram, the most common arrangement is as follows:—

Grams, 20A — 20B — 10 — 5 — 2A — 2B — 1.

Milligrams, 500 — 200 — 100A — 100B — 50 — 20 — 10A — 10B — 5A — 2A — 2B — 1.

Rider, 10 or 12 milligrams.

Some makers depart from the above order in having two one-gram pieces, and one two-gram piece, etc. No particular advantage appears to lie in either system.

One of the pieces is selected as a standard and the deviation of the others therefrom ascertained † It is customary to take the heaviest for this comparison, but for weights to be used in ordinary analyses the one-gram is preferable (page 41).

Placing it in one pan, and in the other those of lesser denominations whose sum nominally equals it, the difference between them, if any, is noted by needle vibrations and if necessary by small weights, with a correction if the arms are of unequal length. We obtain for example .0001 gram which gives the following equation, the figures inclosed in parentheses being those stamped on the weights — their nominal value.

A. 1.000=(500)+(200)+(100A)+(100B)+(50)+(20)+(10A)+(10B)+(5)+(2A)+(2B)+(1)—.0001.

In the same way are found,

B. (500) = (200)+(100A)+(100B)+(50)+(20)+(10A)+(10B)+(5)+(2A)+(2B)+(1)+.0007.

C. (200) = (100A)+(50)+(20)+(10A)+(10B)+(5)+(2A)+(2B)+(1)+.0005.

D. (200) = (100A)+(100B)+.0001.

E. (100A) = (50)+(20)+(10A)+(10B)+(5)+(2A)+(2B)+(1)+.0009.

F. (100A) = (100B)+.0005.

G. (50) = (20)+(10A)+(10B)+(5)+(2A)+(2B)+(1)—.0004.

H. (20) = (10A)+(5)+(2A)+(2B)+(1)+.0006.

I. (20) = (10A)+(10B)+.0002.

J. (10A) = (5)+(2A)+(2B)+(1)+.0002.

K. (10A) = (10B)—.0002.

L. (5) = (2A)+(2B)+(1)+.0001.

M. Rider (10) = (10A)+.0003.

The equations are now to be combined to deduce the actual weight of each piece as compared with the gram taken as normal. Substracting B from A gives

N. 1.000—(500) = (500)—.0008; or (500) = .5004 gram.

Substituting .5004 in equation B and transposing,

O. (200)+(100A)+(100B)+(50)+(20)+(10A)+(10B)+(5)+(2A)+(2B)+(1) = .4997.

Transposing equation C,

P. (200)—(100A)—(50)—(20)—(10A)—(10B)—(5)—(2A)—(2B)—(1) = .0005.

Adding O and P,

Q. 2 (200)+(100B) = .5002.

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* Journ. Chem. Socy. 47—116.

† Crookes' Select Methods, 685; Journ. Amer. Chem. Socy. 1900—144.

Doubling equation D and transposing,

R. 2 (200)—2 (100A)—2 (100B) = .0002.

Subtracting R from Q,

S. 2 (100A)+3 (100B) = .5000.

Multiplying F by 3 gives,

T. 3 (100A)—3 (100B) = .0015.

Adding S and T,

U. 5 (100A) = .5015, or (100A) = .1003.

From F, (100B) = .0998.

And from D, (200) = .2002.

Substituting the value of (100A) in E and transposing,

V. —(50) = (20)+(10A)+(10B)+(5)+(2A)+(2B)+(1)— .0994.

Subtracting V from G,

W. 2 (50) = .0990, or (50) = .0495.

The values of the (20), (10A), (10B), and (5) are calculated in the same way as the above. The weight of the rider is found from M, and weights below .005 gram compared with it. The two-gram weights are tested against the one-gram and its fractions; the five-gram by the twos and one, and so on to the highest of the set.

A table like the following is drawn up and kept in the balance-case.

Grams.	Milligrams.	Milligrams.
(20A) = 19.9997	(500) = .5004	(10B) = .0101
(20B) = 20.0013	(200) = .2002	(5) = .0049
(10) = 10.0002	(100A) = .1003	(2A) = .0019
(5) = 4.9986	(100B) = .0998	(2B) = .0020
(2A) = 2.0002	(50) = .0495	(1) = .0009
(2B) = 2.0008	(20) = .0202	Rider = .0102
(1) = Standard.	(10A) = .0099	

CHAPTER 4.

THE OPERATIONS IN ANALYSIS.

Having the sample pulverized and dried or otherwise prepared, a portion is to be weighed for the analysis.

The amount of material to be used for any given determination depends on several conditions, such as the accuracy of the method employed, the degree of exactness required for the results, the skill of the analyst, and the time allowable. Many of the errors incurred in an analysis affect the result inversely with the weight of substance taken, while on the other hand the smaller the weight the less time is required for evaporations and filtrations, and the more quickly will the analysis be completed.

Of minerals, alloys, crystalline salts and inorganic bodies generally, for constituents present in reasonably large proportions, say five per cent or more, and where the methods are unexceptionable, one gram of a solid or so much of a solution as contains this weight will be found satisfactory as regards both accuracy and speed. A constituent of less than say one per cent calls for a proportionally greater weight of sample, and when it is desired to express centesimally the proportion of one so small as to be ordinarily reported as 'a trace,' 50, 100, or even 200 grams may be required. In ultimate organic analysis from .1 to .5 gram is sufficient, while in proximate organic analysis with questionable methods, from 5 to 50 grams is not excessive. Of gases, 50 and 100 Cc. are standard volumes and gas burettes are generally of one of these capacities. For traces of an important gas in a mixture many litres are drawn through the absorbing medium to obtain a weighable amount of the constituent.

It is seldom necessary to weigh exactly the amount that is prescribed in the method followed; although where many analyses of the same kind are to be made the calculation of the results is somewhat facilitated by taking a fixed or a 'factor' weight; yet the samples may be received by the chemist in such a form (*e. g.*, coarse drillings of a metal) as to make this a more tedious affair than the calculation. However, such matters as these are best left to be decided by the individual.

When an analysis is to be made in duplicate or triplicate, instead of weighing two or three portions of the sample it is often feasible to dissolve one macro-weight and make up the solution to a definite volume with water; then draw out with a pipette such aliquot parts as will contain proper amounts of the substance for analysis. This is especially advantageous when the substance is a mixture of a character that does not admit of fine subdivision or thorough blending, as the greater the weight the more nearly should it represent the original.

The allowable error in weighing the portion for analysis may be taken as one part in one thousand (one milligram per gram) except in the determination of a constituent forming nearly the whole of the substance or where the method is a highly accurate one. That this limit is sufficiently close is manifest when it is considered that a difference of one one-thousandth on the result of the determination of a constituent forming say 50 per cent of the whole is only .05 per cent, decreasing as the proportion of the constituent decreases. In general

in an assay the smaller the proportion of the constituent determined, the less accurate need be the weighing of the substance.

Powders that tend to absorb but little moisture from the air can be weighed in an open watch-glass, using a steel or horn spatula for transferring, or what is handier, a small square of heavy platinum foil sealed in the end of a glass rod. The watch-glass is then held over a beaker or dish and the powder allowed to fall, tapping the edge to loosen any adhering clumps. What little powder remains is brushed down with a clean small camels-hair brush. If the powder is to be introduced into a flask, a wide-stemmed funnel is used, afterward rinsed down with the solvent; a counterpoised metal scoop is better for the purpose than a watch-glass.

Fig. 34. 1/2

The comparatively few powders that are so hygroscopic, efflorescent or volatile as to increase or diminish in weight during the operation sufficiently to affect the accuracy of the analysis are contained in tightly closed vessels, like the light glass-stoppered weighing bottle Fig. 34. The bottle is partly filled and weighed, and approximately the quantity required for the analysis poured out into a beaker; on reweighing, the loss sustained is the weight abstracted. A pair of test-tubes without flanges, one fitting closely in the other, can be substituted for the weighing bottle.

In dealing with a liquid it is usually more convenient to measure a certain volume and calculate its weight from the specific gravity, and this is the usual procedure, the exceptions being where greater exactness is desirable than can be attained with the ordinary appliances for measuring.

A non-volatile liquid may be weighed in a counterpoised beaker or flask into which it is conveniently introduced from a pipette or a test-tube fitted up like a wash bottle (page 97). For quantities less than a gram a short narrow glass tube with one end drawn out to a fine orifice is weighed; a few drops of the liquid are drawn in by suction and held by capillarity during the reweighing, then washed out by the solvent into the vessel for analysis. A pipette for weighing and delivering small volumes of a liquid is shown in Fig. 35.

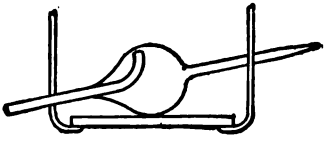

Fig. 35.

When a weighed quantity of an aqueous solution is to be evaporated in a tared dish, a flask containing the liquid is weighed, about the required volume poured out into the dish, and the flask reweighed. This plan avoids any error that would arise from evaporation were the liquid weighed in an open vessel.

A very hygroscopic liquid, such as Nordhausen sulfuric acid, is drawn into a thin tared glass bulb with capillary prolongs and the ends of the capillary tubes sealed by the blowpipe. The bulb is reweighed, then dropped into a bottle containing the solvent, and the bottle shaken until the bulb breaks.

A volatile liquid is held in a weighing-tube which is afterward dropped into the solvent before removing the stopper. Or a thin glass bulb with a capillary stem is warmed and the stem held in the liquid, a small volume entering as the bulb cools; this is boiled until the air is expelled, and the stem is again submerged when the bulb will fill completely and may be weighed. It is dropped into the solvent and crushed by a glass rod.

SOLUTION.

"Solutions may be defined as homogeneous mixtures which cannot be separated into their constituent parts by mechanical means, the proportion between the parts being continuously variable between certain limits, with

a corresponding continuous variation in properties." (Whetham). In a broad sense the term includes the union of either a solid, liquid or gas with any one of the three, but popularly speaking, refers rather to the disappearance of a solid or a gas in a liquid. When no more of a solid can be taken up and permanently held the solution is said to be 'saturated'; with most salts an unstable stronger one may be obtained, called 'supersaturated'. In analysis only comparatively dilute solutions are the rule.

A strict construction of the term 'insoluble' implies an attribute of matter of which we can furnish no unqualified example, but as commonly used it signifies that the substance in question is not affected by a given solvent to such a degree as to *materially* decrease its mass. And so the word 'soluble' comprehends not only the bodies dissolving easily and abundantly, but those requiring a prolonged digestion with a large proportion of the solvent as well, one class merging into the other. Calcium hydrate has been proposed as the dividing line, it dissolving in about 584 parts of water at 15° C.

Solvents. It is at least a matter of convenience to consider all solutions as involving chemical decomposition or combination, whether the substance can or cannot be recovered unaltered on evaporation of the solvent. With the exception of a few solids, like carbon, and some gases, little difficulty is experienced in finding a solvent for every substance, and, in general, this is the first step in every analysis. *Water* dissolves most crystalline salts and acids, the sugars, alkali soaps, tannins, alkaloidal salts, gums, albumenoids, and starches (when hot); the *inorganic acids*, metals, their oxides and hydrates, and many native and artificial compounds; *alcohol*, most deliquescent salts, the alkaloids, tannins, resins, essential oils, chlorophyll, and many organic acids; *ether*, *chloroform*, and *ligroin*, the fixed oils and fats, some resins, and the alkaloids; *glycerol*, many inorganic salts, the gums, starch, albumin, pepsin, tannin, and many of the analine dyes; *carbon disulfide*, phosphorus and sulfur; *acetone*, the camphors and fixed oils, etc.

Special solvents are employed (1), when those of general application are ineffectual; as concentrated sulfuric acid for ferrochrome, alizarin, and indigotin; (2), where perduction * or reduction of an insoluble solid changes it to a soluble combination; (3), to induce polymerization, hydrolysis, or saponification; (4), to hasten the time of solution by some chemical reaction or by catalysis; or (5), to prevent loss of a constituent or reaction-product through volatilization.

An acquaintance with the composition and solubility in various menstrua of the substance under examination should be gained before the quantitative analysis is proceeded with, and if a choice of solvents is allowed, the one is selected that is best adapted to the reactions in the several determinations following, or will the least interfere with them.

Usually the solvent is a clear liquid, but occasionally a solid in mass or powder is incorporated therewith to produce some specific effect without the introduction of an acid or soluble base. Occasionally one meets a precipitate or solid body that best dissolves when suspended in water and a gas passed through the mixture. Oxygenation is sometimes brought about by passing a current of air through the water.

In general an amount of solvent in considerable excess of that actually required for solution is employed. Exceptions are where a clear solution obtained with a limited proportion of solvent becomes cloudy on dilution with a further portion, from separation of part of the matter dissolved. However, as

* Journ. Franklin Inst. 1901—201.

a rule it is well to restrict the amount of solvent to a moderate excess, as more than this is often objectionable for several reasons.

The concentration of a solution or mixture used as a solvent is a matter of importance. The solvent capacity of many is at a maximum at a certain concentration, less effective when weaker or stronger; for example, silver chloride in ammonia, gliadin in dilute alcohol, keratin in solution of potassium hydrate, etc. Of a mixture of two liquids the solvent power toward a given solid depends not only on the rate of solubility in each, but on the predominance of one or the other in the mixture as well.

An acid of medium strength will generally give better results than if more concentrated, as many metals and their compounds are insoluble in a strong, though readily so in a dilute acid. Immersed in strong nitric acid, iron becomes passive and insoluble, said to be protected by an impervious layer of nitrate or oxide formed on the surface; when strong hydrochloric acid is used to decompose a silicate, the liberated silica (leucone) gelatinizes at once and encysts particles of the unattacked mineral, shielding them from contact with the acid; etc. So as a rule one should employ as dilute a solvent as will accomplish the purpose unless otherwise directed for special reasons, always recognizing that during the operation the acid becomes continually weaker by neutralization or decomposition. Practically from five to fifteen cubic centimeters of either of the mineral acids, concentrated or diluted with water as directed, is sufficient to dissolve one gram of a metal or its compounds.

As a rule solution is promoted by heating the solvent. A specific formula for the solubility at different temperatures may be deduced from the formula $S = A + Bt + Ct^2 + Dt^3$, where S is the proportion of solid dissolved; A, the solubility at zero Cent.; t, the temperature; and B, C, and D, empirical coefficients determined by experiment. The solubility-curves of a few salts are nearly straight lines, while a few compounds, such as calcium butyrate, show a decreasing solubility with increase of temperature.

Although heating a solvent is usually allowable and advantageous in point of time required for solution, yet a boiling heat is often interdicted on account of the decomposition of the solute or volatilization of some constituent. Heat should not be applied to a concentrated volatile acid or alkali to such a degree that it becomes weakened by the escape of its gas before solution is accomplished; a temperature of 40° to 60° will usually give the best results.

Solution is also promoted by finely dividing the solid to increase the surface exposed to the solvent, or in the case of a liquid by the mixture of another liquid to form a semi-solution or emulsion. Thus a slag, but slowly and imperfectly acted on by an acid when in a moderately fine powder, is readily dissolved when it occurs disseminated through an unrefined metal, and the metal treated with an acid.

Fig. 36.

Powders inclined to agglutinate are best mixed with some granular inert solid such as sand or quartz powder, that tends to keep the particles separated.

The time allowed for a solution is of no consequence except for organic substances where ferments or bacteria may effect changes. Sterilization by heat or germicides may be advisable where long contact with the solvent is essential.

On dissolving one of the higher metallic oxides in an acid a partial reduction to the compound corresponding to the most stable oxide takes place. A total transformation generally follows boiling for a time, or may be accomplished at once by the addition of some reducing agent. Rarely, a sol-

vent may be found that will dissolve a higher oxide without reduction (e. g. glacial acetic acid for lead peroxide). Metals and oxides lower than the normal may be dissolved without change of valence in a non-oxidizing acid with exclusion of air.

The layer of fluid in contact with a powder lying at the bottom of a vessel soon becomes saturated, and so a frequent and sometimes continual stirring or shaking is necessary. A mechanical stirrer saves time and labor with a substance slow to dissolve; it is simply a bent glass rod, Fig. 36, rapidly turned by a small electric or water motor, a toy steam engine, or a light sheet-metal fan driven by a blast of air. Another means is to inclose the powder in a porous container such as a linen bag or a cage of platinum gauze, Fig. 37, suspended just below the surface of the solvent; the specifically heavier solution as it sinks to the bottom of the beaker displaces the virgin solvent and establishes a current through the container; or if oxidation is not to be feared, a stream of air may be forced into the liquid through a narrow glass tube reaching to the bottom of the vessel, the stream of bubbles diffusing the solid through the solvent.

Fig. 37.

Vessels for solution. The solution may take place in a beaker-glass, dish or flask. Beakers are made in two shapes, the tall or ordinary form about two diameters high, and the Griffen, somewhat wider in proportion. The former is better for dissolving metals, carbonates and the like where gases are evolved, while the latter is more convenient for evaporations and precipitations. Sizes may be purchased from 15 to 4,000 Cc. capacity, those holding from 150 to 600 Cc. being of more general use. They are covered with watch-glasses or round glass plates of slightly greater diameter than the top of the beaker for the exclusion of dust.

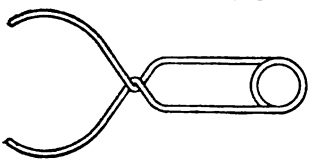

Fig. 38. 1/6

Beakers containing hot liquids are conveniently handled by the use of a tong, Fig. 38, made of spring brass wire. Langmuir proposes the use of a leather strap an inch wide by twenty inches long passed around the beaker and the ends held between the thumb and finger.

Flat bottomed, triangular, or Erlenmyer flasks, Fig. 39, are preferred by some to beakers for general work, the sizes grading about the same. Large test tubes about one inch in diameter by twelve or more inches in length serve well for dissolving metals in acids and similar operations, since losses from bubbles of gas and contact with air are prevented, and offensive gases may be led into the open air by a cork and tubing.

Fig. 39.

All glassware must be of a composition free from lead and designed to resist the solvent action of water and solutions, and well annealed to stand heating without fracture. As glass and porcelain are corroded by hydrofluoric acid, in solution or generated when a fluoride is dissolved in an acid, a platinum dish or large crucible is substituted when dealing with such material. On the other hand, a platinum dish cannot be used for

hot liquids containing or evolving chlorine or bromine, such as nitro-hydrochloric acid, a nitrate or bromate with hydrochloric acid, etc.

Fig. 40 A.

Since solution takes place more readily as a rule when the solvent is heated, it is often an advantage to raise the temperature above its boiling point which can be done by preventing the escape of its vapor.

A bottle of heavy glass closed with a well-ground glass stopper secured by a clamp, Fig. 40, or a porcelain cap with a soft rubber ring, Fig. 40A, may be used for this purpose; it is also of service where it is desired to heat without loss a volatile liquid or one containing or evolving a volatile constituent, or to hasten a chemical change in a solution that occurs but slowly at a boiling temperature. For greater safety the mouth of the flask may be expanded to form a gutter around the stopper; the gutter being filled with a suitable liquid entraps any vapor that may escape between the neck of the flask and the stopper.

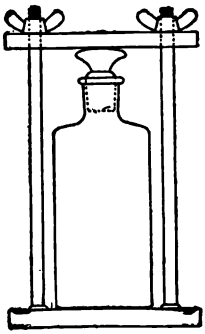

Fig. 40. 1/4

Allen advises that a heavy flask be closed by a rubber stopper, wired down, through which passes the short leg of a glass tube bent twice at right angles, the longer leg dipping into a tall cylinder filled with mercury. The distance the mercury is depressed in the tube shows the pressure in the flask, thirty inches corresponding to an additional atmosphere. The flask is heated in a saline solution of a suitable boiling point.

An autoclave or miniature Papin's digester, a kettle of heavy sheet metal with a steam-tight cover and pressure-gauge, can be used for the extraction of animal or vegetable matter at a heat above the boiling point of water under atmospheric pressure.

Many refractory minerals are dissolved when digested with an acid at an elevated temperature. A thick-glass tube, Fig. 41, is sealed at A, the powdered mineral and acid introduced, the upper end drawn out into a narrow prolong BC, and the end sealed by a blowpipe. The tube is laid horizontally in a special form of air-bath and heated for several hours to a temperature considerably above 100°. After cooling, the tube is held upright and C softened in a blowpipe flame, when any gas evolved during the solution forces its way through the plastic glass; the prolong is then cut off and the solution poured out.

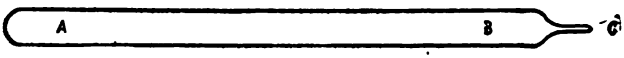

Fig. 41.

When it is desired to boil a solvent without its volume being diminished, a condenser may be attached as in A, Fig. 42; the lower end passes through the cork of the flask, and the vapor rising into the inner tube is condensed and the liquid drops back. This position of the condenser is termed 'inverted,' 'reversed,' or 'reflux.' A simpler, though less effective contrivance, is a small U-tube of thin glass cooled by transmitted water, hanging in the neck of the flask B.

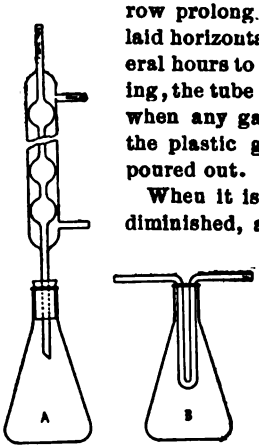

Fig. 42.

Goeckel* describes a cover for a lipless beaker, in the

* Zeits. angew 1899—494.

to of a glass bulb, conical below, of somewhat greater diameter than the beaker; a stream of cold water is conducted through the bulb by two sealed-in tubes.

Where a stream of water is not available, a fair degree of condensation may be had by inserting the lower end of an open glass tube through the cork of the flask and supporting the tube in a nearly vertical position. The tube should be several feet long (less unwieldy if coiled into a spiral), and the glass thin since the air is the only refrigerant.

An apparatus allowing the treatment of a substance in an open dish with a volatile solvent is shown in section in Fig. 43.* The heavy line is a thin cast iron cup whose periphery has the form of a gutter, and is heated by a burner below. The evaporating dish containing the solvent and substance is placed in the depression of the cup, a thin bell-glass with open top set in the gutter, and a little mercury poured in to make a vapor-tight joint. The mouth of the bell-jar is closed by a cork carrying a reversed condenser. Since the bell-jar becomes heated, no condensation occurs on the interior surface. After solution, if it is desired to distill most or all of the solvent, a slant condenser is substituted for the reversed condenser.

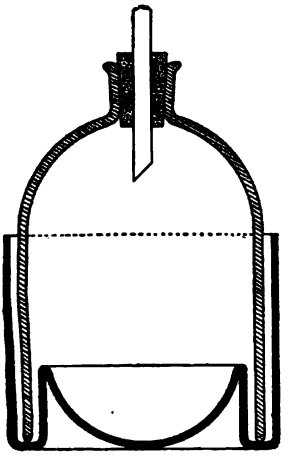

Fig. 43.

In dissolving a metal or compound it is often essential that contact with the air, or entrance of dust and laboratory fumes, be prevented. The solution may take place in a flask closed by a cork or rubber stopper through which pass two glass tubes transmitting a current of some non-oxidizing gas, such as nitrogen or carbonic acid.

Where an acid is the solvent, the flask may be connected by a cork and tubing to a beaker containing a solution of sodium bicarbonate. A little sodium bicarbonate is placed in the flask with the substance to be dissolved, the acid poured on, and the flask stoppered. Heat is applied until solution is complete, and on cooling bicarbonate solution is drawn back into the flask and generates sufficient carbon dioxide to prevent entrance of air. Water boiled free from air is used to dilute the solution.

Offensive or noxious gases or vapors evolved during a solution should be led into the open air by operating under a "hood" or draught-chamber, or by dissolving in a flask provided with a cork (or rubber stopper if unobjectionable) in which is fitted a glass tube connected by rubber tubing to another passing through a hole in a window-frame.

Percolation. Certain varieties of vegetable matter and many drugs yield their active principles to solvents with such reluctance that a prolonged digestion and a large volume of solvent is needed. The advantage of the process of 'percolation' over simple digestion is that the constituents more difficult of extraction are continually brought in contact with the pure solvent. The percolator, Fig. 44, is a glass or metal cylinder contracted to a small outlet at the bottom; in this is fitted a cork holding a short glass tube over the lower end of which is drawn a narrow rubber tube leading to the receiving flask. Above the

* Blyth, Foods, Their Composition and Analysis, 70.

cork the neck of the percolator is plugged with cotton, and over this is a layer of clean sand. The powdered bark, leaves, etc., are introduced either loosely or tightly packed according to their permeability and other properties, nearly filling the percolator. The solvent, cold or hot as required, is then poured in, the rubber tube compressed by a pinchcock, and the mixture allowed to macerate or digest for several hours. The pinchcock is released and the liquid run out. More of the solvent is then run through, becoming the more impregnated as it descends, until the color or a qualitative test shows that the extraction is complete.

Fig. 44

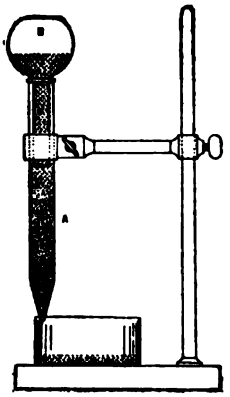

Fig. 45. 1/8

A simple form of percolator that requires no attention after it has been started is shown in Fig. 45. The test-tube A has a small orifice at the bottom, and is packed to the depth of an inch or more with cotton; on this rests the drug. The narrow-necked flask B is filled with the solvent and inverted into A, the solvent being retained in B by atmospheric pressure and fed into A only as fast as air can enter and displace it.

The ratio of the height of the percolator to the diameter is governed by the character of the drug and the degree of comminution, but obviously the longer and narrower, the less solvent is required for complete exhaustion, and this fact is practically applied in another way in the processes of 'repercolation' and 'sectional percolation.'

In many powders, especially those rich in extractive, channels may form through which the solvent passes in preference, greatly augmenting the quantity of solvent required for thorough extraction. An occasional stirring of the powder will break up any channels formed; or the powder may be mixed with a quantity of shredded filter paper before filling the percolator.

Continuous percolation. In an 'extraction apparatus' a still more thorough exhaustion is had with a minimum of solvent. Many forms have been proposed, all on the same principle however, namely, that the percolate is received in a heated flask from which the solvent distills leaving the non-volatile extractive; the vapor is condensed and returns to the percolator.

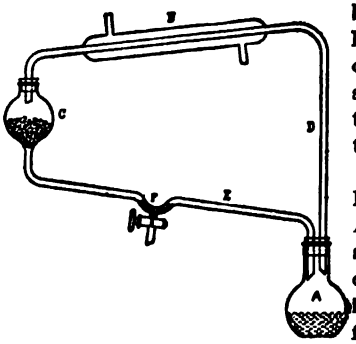

Fig. 46.

Raikow's apparatus is shown in Fig. 46. It consists of three parts, a distilling flask A, partly filled with ether or other volatile solvent; a condenser B; and a funnel C containing the powder to be extracted resting on a plug of cotton in the stem. The flask A is heated on a water-bath and the vapor of the boiling ether rises in the tube D. The inclined portion of D is surrounded by a larger tube B through which circulates a stream of cold water; here the ether vapor is condensed and drops upon the substance in C, and after percolating it, runs back into A by way of

the tube E. Thus the circuit of the ether goes on continuously until all the extractive has collected in A. To prevent the vapor of the ether from passing into C, the tube E has a trap at F.

The most popular form of extractor for general work is that of Soxhlet,* Fig. 47. The vapor from a flask A rises through the tubes B and C into the condenser, the form shown being two concentric spheres of glass or thin metal, the inner one cooled by water flowing through it entering at F. The vapor is condensed on the surface of E and drops upon the substance in the cup G, contained in a plaited filter, a thimble of filter paper, or a tube closed with a plug of cotton or glass wool. When G is filled to the dotted line, the tube H acts as the longer leg of a syphon and transfers all the liquid to the flask A. After the extraction, the substance may be removed from G, a short test-tube substituted for it, and the ether distilled up into the test-tube, leaving the extractive in the flask ready for weighing. Disadvantages of the Soxhlet apparatus are fragility, the danger of carrying some of a finely powdered substance into the flask during the rapid outflow of the solvent, and relatively high cost. Various modifications have been proposed.

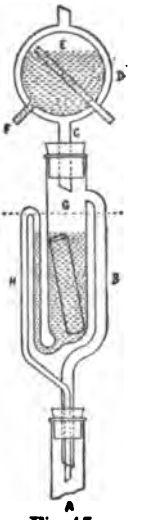

Fig 47.

A simple form is shown in Fig. 48.† A large test-tube A contains the solvent and is closed at the top by a metal cap B. The condensor is a tube made up of a series of double cones of sheet metal cooled by water entering at E and leaving a D. Below the tube hangs a porcelain crucible with a perforated bottom containing the substance to be extracted.

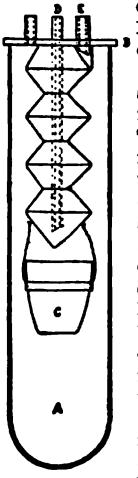

Fig. 48 1/4

Lumsden ‡ describes an apparatus suitable as well for the finer powders as the coarsely granular, the solvent being forced through the mass by vapor pressure. The flask *a*, Fig. 49, of about 80 cubic centimeters capacity, is fitted with a cork through which projects the contracted end of the exhaustion tube *c*. The tube contains the sample held between plugs of glass-wool. From the top of *c* passes a tube through a condenser *d* nearly to the bottom of a flask *b*. The flask is immersed in a jar of water kept at a practically uniform temperature by the overflow of the condenser. The cork of *b* is notched to prevent the pressure in the apparatus from rising above atmospheric.

The flask *b* is half filled with ether and a few cubic centimeters poured into *a*. The apparatus is connected as shown and *a* immersed in a beaker of hot water; the ether vapor generated expels the air from the apparatus. Then *a* is placed in cold water, the vacuum formed by the condensation of the inclosed vapor drawing the ether from *b* into *a* via the material in *c*. Afterward *a* is transferred from cold to hot water, causing the ether to return to *b*. The cycle is continued until the exhaustion is complete.

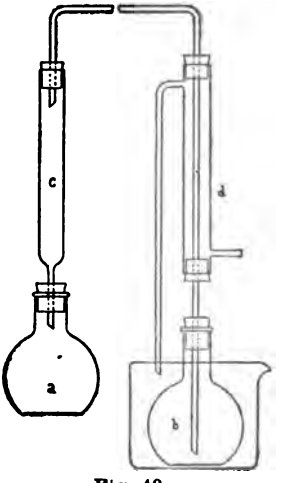

Fig. 49.

In the apparatus of Wollny, Fig. 50, the powder to be extracted is continually permeated by the hot vapor of the solvent and intermittently drenched with small volumes

* Chem. News, 1888—1—56, 91, and 235, and 1891—1—86; Journ. Amer. Chem. Socy. 1901—338.

† Journ. Amer. Chem. Socy. 1893—121.

‡ Chem. News 1888—130.

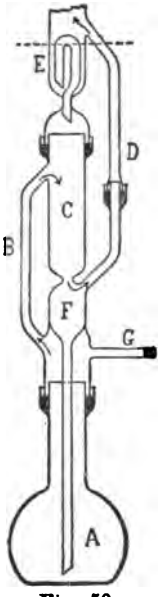

Fig. 50.

of the liquid. The solvent is contained in the flask A and the substance in C; as the solvent boils the vapor rises in B, passes down through the substance into F, thence rises through D into a condenser attached above E. The condensed liquid drops into E filling it to the level of the dotted line, when the inclosed syphon transfers the entire contents into C. After percolating the substance the solvent runs through F into A. If the extractive is somewhat volatile or affected by the temperature of the boiling solvent, the side tube G may be opened and vapor generated in another flask inducted.

Ordinary corks contain resin, etc., soluble in ether and like fluids, and rubber is also attacked, so that both are objectionable for connections exposed to these fluids or their vapors. The three connections shown in the figure are made in a different way, namely by a 'mercury seal'. The lower tube has a short tube of larger diameter fused on near the top forming a gutter in which stands the bottom of the upper-tube. The gutter is nearly filled with mercury making a gas-tight trap, the weight of the mercury withstanding the slight increase over atmospheric pressure of the inclosed vapor.

An apparatus for the extraction of oil from seeds is due to Lehmann. It is a small conical mill in which the seeds are ground fine. After removing the handle of the interior cone, the entire mill is placed in a large extraction apparatus and the oil dissolved out.*

Instead of packing the sample in the exhaustion tube of an apparatus, it may be held in a plaited filter, or an 'extraction thimble', a narrow, seamless cup made of a special quality of filter paper. Many substances are more quickly and easily extracted if mixed with an insoluble powder. An emulsion of a fatty matter in water or an aqueous solution may be imbibed in a tight roll of filter paper, which after drying is extracted directly by ether or gasoline.

An extraction will consume from an hour to a day or longer, according to the nature of the substance and the percentage of extractive it contains. The length of time required is not a great objection as the apparatus is automatic and needs little attention, but it can be inferred only by experience as there is usually no provision short of disconnecting the apparatus to ascertain when the extraction is complete. It has been proposed to provide a tap below the percolator (as at F, Fig. 46) that a small amount of the solvent may be drawn off occasionally and tested by evaporation.

The process of extraction finds use principally in dissolving fats, gums, alkaloids, etc., from accompanying insoluble matters. The solvents are commonly ether, chloroform, gasoline, alcohol and benzene, less frequently water and volatile acids and ammonia. In most cases the solvents have a boiling point of less than 100°, though for a few extractions such liquids as anilin and napthalin are more efficacious.

Of the organic solvents, ether, gasoline and alcohol are most in use. Commercial ether always contains some water and alcohol and must be purified by washing out the alcohol with water, and removing the water by distillation from a hygroscopic solid. Gasoline, also known as petroleum ether and ligroin, is a mixture of the hydrocarbons of the second fraction of the distillation of petroleum. Commercial gasoline is unsuitable for extractions; the grade of a density of 87° Baume is distilled fractionally, rejecting all that comes over below 40° and above 60° Cent. For some purposes other fractions of the distillate are more suitable, as the higher the boiling point the higher the temperature of the solvent in contact with the substance to be extracted. In any case the narrower the limits of temperature between which the fraction begins

* Chem. News, 1890—1—15.

to boil and completely volatilizes, the more regularly will the process of extraction proceed. When using a mixture of liquids, such as diluted alcohol, or a solution of a gas, it must be remembered that the vapor has generally a different composition from the original liquid.

Insoluble inorganic substances can usually be transformed to a soluble state or combination by some preliminary igneous treatment.

Simple ignition may alter the form of combination of an insoluble material so as to allow a subsequent partial or complete solution in an acid or alkali; thus the mineral talc, $Mg_3H_2Si_4O_{12} = 3MgSiO_3 + H_2O + SiO_2$, the silica becoming soluble in a solution of sodium carbonate. Several minerals can be made completely soluble in this way.

Ignition in a current of air or oxygen will oxidize sulphur and burn out bituminous or other organic matter that may hinder solution, and some of the rare metals, indifferent to all acids, calcine to soluble oxides. Ignition in hydrogen reduces higher to lower oxides, and some oxides to the metallic state. At a moderate heat the vapor of sulphur or carbon disulfide forms volatile or fixed sulfides with many metals and alloys, and a current of air loaded with the vapor of bromine has been proposed for the decomposition of certain native sulfides.

Fluxing. The solvent or decomposing power of a reagent is much greater when applied above the temperature of fusion than when in aqueous solution, and many insoluble compounds are changed to a soluble form by fluxing. The choice of a flux depends mainly on the composition of the substance to be treated, though differences in aggregation or crystalline character of the sample may lead to the substitution of a flux more effective though perhaps less suitable chemically.

Native silica and titanic acid and many silicates react with the oxide of potassium or sodium at a melting heat, the product being soluble in water or in acid. A large excess of sodium carbonate is generally the flux, the silica, alumina, etc., replacing the carbon dioxide radical, while the bases are converted into oxides or carbonates.

Other fluxes in less common use are sodium carbonate with potassium nitrate; sodium hydrate alone or with sodium nitrate, sulphur or charcoal; sodium peroxide; sodium thiosulfate; potassium or sodium pyrosulfate; boric acid; sodium fluoride; and borax-glass; also soda-lime and various metallic oxides as sinters.

The fusion is nearly always made in a platinum crucible, though with a flux of a caustic alkali or baryta a silver or gold crucible is better because less attacked. The mineral to be decomposed is ground to a fine powder and mixed with a large excess of the flux also in powder, and the mixture placed in a crucible so large that it is not more than half filled. The crucible is covered and supported on a platinum triangle resting on the ring of a retort-stand, and heated by a burner, gently at first, finally to complete fusion. A large Bunsen burner or a blast-lamp furnishes sufficient heat for the fusion which is known to be complete when the mass settles down to a quiet liquid evolving no more gas.

When the crucible and contents have completely cooled the solidified lump is sometimes difficult to remove, but if the crucible be inclined as far as may be while the contents are still liquid and solidification take place in that position, the two will readily part in most cases. Or a heavy platinum wire

may be plunged into the fusion, and after solidification, the crucible hung over a platinum triangle and heated by a strong flame until the crucible separates from the mass within and falls into the triangle. The projecting end of the wire is then bent and hooked over the edge of a beaker so as to suspend the lump just below the surface of the solvent in the beaker.

The volume of a gas absorbed by a liquid when no apparent chemical combination takes place, depends on the nature of the gas and liquid, and varies directly with the pressure and inversely with the temperature of the liquid. Most gases dissolve in water according to the equation $V = a + bt + ct^2$, where V is the volume dissolved in a unit weight of water; t, the temperature of the water; and a, b, and c, empirical coefficients determined by experiment.

The ready absorption in a liquid of a gas or some one of a mixture of gases is favored by a low temperature, a high coefficient of solubility, and their protracted and intimate contact. Usually, only a partial absorption is had during the bubbling of a gas through a liquid, completed, however, if it be allowed to remain standing over the surface for a time; therefore the space in the vessel unoccupied by the absorbent should be ample to retain the gas for a considerable period, the current being reasonably slow. And in rising through a liquid the smaller the bubbles and the more obstructed their path, the more ready and complete the absorption. With this object in view, many forms of apparatus have been devised.

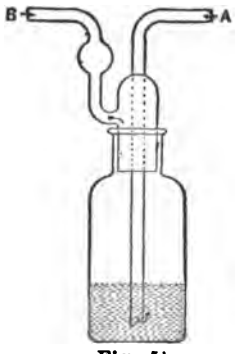

Fig. 51.

The most common is the well-known gas-washing bottle, of which one form is shown in Fig. 51, the gas entering at A, bubbling through the liquid, and passing out through B. Usually two or more are joined tandem.

In Fig. 52 is shown a form due to Thoerner. A large glass tube is slightly inclined from the horizontal; the gas enters from the large bulb in separate bubbles each rising along the upper part of the tube to the exit. Winkler's modification is more compact, the tube being coiled into a spiral; while Meyer would replace the straight tube by a series of small bulbs.

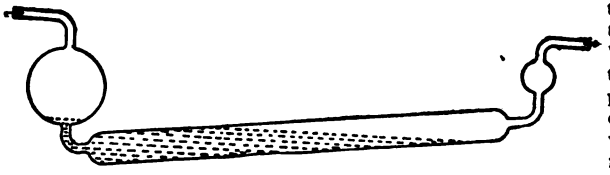
Fig. 52.

Emmerling's tube, Fig. 53, is on the principle of the Glover tower; the gas entering at A wanders through a column B of broken glass or glass beads drenched with the absorbing fluid dripping from the funnel C, and finally emerges from D; as the absorbent collects in B it is occasionally tapped out into a flask below.

Usually a solid granular absorbent is held in a large glass tube bent in the form of the letter U, the openings being fitted with corks through which pass narrow glass tubes; or the stoppers may be of glass, acting as stop-cocks when turned at an angle, Fig. 54.

There are a few instances where a determination of a compound in solution may be made by finding the weight of an insoluble solid that reacts with the

compound and enters into solution. Examples are the determination of aceton in urine, done by boiling a measured quantity of urine with mercuric oxide and afterward determining the weight of mercury that has passed into solution; when an acetyl derivative dissolved in water is boiled for some hours with magnesia there is formed magnesium acetate which dissolves and can be determined gravimetrically; commercial pepsin is valued by the weight of white of egg (coagulated albumen) that is dissolved by an aqueous solution of the pepsin, etc. The method is usually applied in cases where the direct determination of a compound is difficult, and is not very reliable for complex solutions.

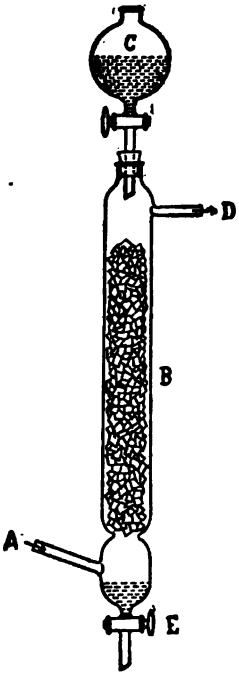

Fig. 53.

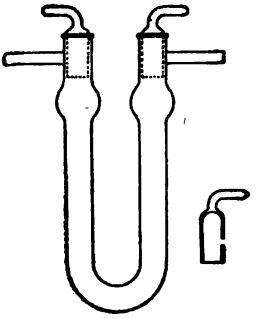
Fig. 54.

EVAPORATION — DISTILLATION — SUBLIMATION.

Evaporation of a liquid is resorted to (1), for reducing the volume when too dilute for certain operations or convenient manipulation; (2) to expel some volatile compound whose presence is objectionable for a subsequent operation; (3), to obtain a dissolved body in the solid form; or (4), to change the aggregation of a suspended precipitate or residue from solution to one more compact and manageable in filtration.

Practically the rate at which evaporation proceeds is determined by the temperature of the liquid, the extent of surface exposed, and the rapidity with which the vapor is displaced by air, and is also influenced by the density of the liquid, the amount of solid matter in solution, and the pressure and humidity of the atmosphere.

For economy in point of time an evaporation is conducted as rapidly as may be done without danger of loss by projection from the bursting bubbles of steam.

A moderately dilute solution is most quickly concentrated in a porcelain or platinum dish over a low flame, heating nearly or quite to gentle ebullition. The dish is supported at the proper height above the burner by the ring of an iron retort stand. If the evaporation is made in a beaker or flask the support is a heated metal or soapstone plate or a sheet of wire gauze covering a retort-stand ring.

Fig. 55.

One of the many forms of hot-plate is illustrated in Fig. 55; it is a metal plate, preferably of cast iron, about one-eighth inch in thickness, supported on legs of a length to bring the plate a few inches above the top of the burner. A flask or porcelain dish may be supported an inch or more above the plate by a ring of tin-plate of slightly less diameter.

A shallow iron dish filled with clean sand (sand-bath) supported on the ring of a retort-stand transmits a more uniform heat than the plate and lessens the danger following the breaking of a vessel standing on it, but has the drawback that the sand tends to scratch glassware, making it more liable to crack.

In the 'electric hot plate' * is applied the moderate and uniform heat diffused when a current of electricity is passed through a wire inadequate in section for its conduction. It is essentially a form of rheostat in the shape of a shallow cast iron box filled with magnesia in which is imbedded a coil of fine nickel wire. Where a laboratory is fitted with incandescent lights, wires may be run from a socket, and the amperage of the current regulated by a resistance coil so as to give any temperature up to one capable of gently boiling water in a covered vessel.

As a source of heat the Bunsen burner shown in section in Fig. 56 provides a clean smokeless flame under perfect control. Coal gas entering at A emerges from a fine hole in the jet B, and rising in the tube C carries with it a stream of air drawn in at the holes D D; the mixture burns at F with a conical blue flame surrounded by an almost invisible mantle. The highest temperature is just above the point of the cone which should be sharply defined. Should the openings D D admit too great a proportion of air, the mixture will refuse to burn, while too small a proportion makes the flame luminous and smoky (though not less calorific †); so the supply of air is regulated by turning a loose sleeve E encircling the burner and having holes corresponding to D D. The burner is connected to a gas tap by rubber tubing.

Fig. 56.

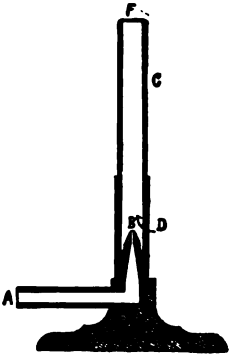

Fig. 56.

A modification of the above has a stopcock at the base for controlling the flow of gas into the burner, simultaneously admitting the proper proportion of air to deluminate the flame.

A low or dwarf form is shown in Fig 57. It is less liable to be injured by the drippings from solutions that have a tendency to boil up and overflow the evaporating dish.

Fig. 57. $^1/_4$

When the gas is turned low and the burner exposed to draughts, the small flame is liable to drop in the tube C and burn at B. This may be prevented by reducing the size of the orifice of C by the insertion of a short piece of glass tubing with the upper edge expanded to rest on F. A burner is made with an arrangement to turn off the gas when this happens, on the principle that when the tube C becomes heated by the flame at B it expands and releases the upper end of a weighted lever connected with a stopcock at the base of the burner admitting the gas; the lever falls, closing the stopcock.

Gasoline-gas burners. Special forms of Bunsen burners have been designed for the highly carburetted gas made by loading air with the vapors of the lighter petroleum distillates. The carburetter (a closed tank on the principle of a gas-washing bottle, Fig. 51) is filled with a high degree gasoline and connected with an air pump. The air bubbling through the gasoline takes up at first mainly the lightest of the mixed hydrocarbons and

* Journ. Amer. Chem. Socy. 1897—790.

† Journ. of Gas Lighting, 38—878.

enters the burner so rich in their vapors that not enough air can be drawn in through D D to prevent the separation of free carbon in the flame. After a time the lightest fractions of the gasoline having been carried off, those of medium density are taken up by the air yielding an entirely satisfactory flame in an ordinary Bunsen. Finally only the least volatile fractions are left and the gas refuses to burn even when D D are entirely closed, and the carburetter must be emptied and recharged.

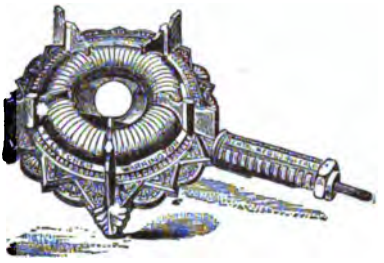

Fig. 58.

The special burners mentioned above endeavor to obviate the smoky flame of the first issue of a newly filled carburetter by lessening the volume of gas passing through B, Fig. 56, while maintaining its normal pressure. But an ordinary Bunsen burns satisfactorily when an auxiliary blast of air is led from the air pump of the gas machine and introduced into the rubber tube leading to the burner or into the gas-pipe leading from the carburetter, regulating the volume inducted by means of a valve or stop-cock.

The ordinary Bunsen is ill adapted for heating a dish directly since the heat is concentrated around one point. A burner with many small flames, such as the 'radial burner' shown in Fig. 58, distributes the heat over the bottom of the dish and diminishes the tendency to explosive boiling. An inverted Bunsen clamped above the dish, the flame nearly reaching the liquid, hastens an evaporation to a remarkable extent and diminishes any tendency to boil over.*

Substitutes for gas. If not provided in a laboratory, or where there is required a flame giving off no sulfurous gases, some form of an alcohol or gasoline lamp may be substituted. The Berzilius alcohol lamp is so well known as to need no description.

Of the several forms of gasoline lamps, that of Kellogg can be highly recommended. It is constructed on the principle of the common gasoline stove, the burner having three movable tips affording different sized Bunsen flames, the largest being almost equal in heating effect to a blast-lamp; there are also rose and wing-top attachments. With reasonable care the lamp is perfectly safe.

Water-bath. With more concentrated solutions it is safer, though less expeditious, to evaporate by steam heat in a "water-bath." The most common form is a hemispherical copper, aluminum, or porcelain dish, Fig. 59, covered by a series of concentric rings that can be removed to provide holes of various sizes to support evaporating dishes and beakers. The bath is half filled with water, and may be connected to a constant water-level (page 27) with advantage.† A glass crystallizing dish half filled with water and heated on the hot plate is a substitute more sightly than corroded copper; the dishes can be purchased in nests, the sizes grading from 2.5 to 8.5 inches in diameter.

Fig. 59. $^1/_4$–$^1/_8$

For the technical laboratory may be provided a large rectangular copper box, the top having a number of holes fitted with rings allowing several evaporations to be carried on at one time; it is usually heated by steam entering from a steam pipe at the side, the condensed water led off through a pipe at the bottom.‡

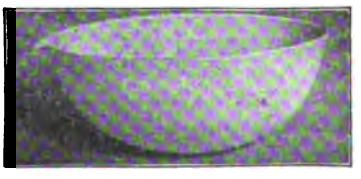

Fig. 60.

* Chem. News, 1888—1—250.

† Chem. News, 1889—2— 250 and 269.

‡ Jour. Anal. Chem. 3—269.

Vessels for evaporation. Evaporating dishes, Fig. 60, are made of thin glazed porcelain of the shape of a segment of a sphere or with a flat bottom, the various sizes holding from 30 to 1,000 cc. or more. They allow a more rapid evaporation than a beaker or flask by reason of the greater surface of liquid and less condensation of steam on the interior, and also withstand more sudden changes of temperature than glass, are less fragile, and less attacked by solutions. Casseroles, Fig. 61, are of a greater depth in proportion to the diameter and are provided with porcelain or wooden handles by which they are more comfortably handled when filled with hot liquids.

Platinum dishes are highly desirable for solutions of the caustic and carbonated alkalies, and indispensable for evaporations of liquids containing hydrofluoric acid. Though rather costly, they last indefinitely if given proper care. The edge of the dish may be left straight or better curled outwardly over a platinum wire ring, stiffening the dish and making it easier to handle when filled with a liquid. Silver and nickel basins can be used for solutions of the caustic alkalies.

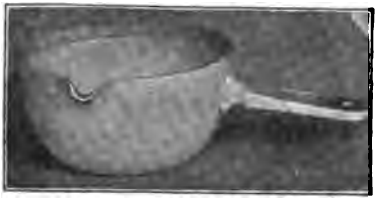

Fig. 61.

A fluid evolving a gas on heating is best concentrated in a capacious wide mouthed flask or tall beaker, and the temperature raised slowly and cautiously. A solution containing an easily oxidizable compound can hardly be concentrated in a reasonable time without some oxidation taking place; it is best conducted in a flask through which passes a current of hydrogen or carbon dioxide.

Small volumes of liquid may be evaporated in vacuo by attaching the flask to a filter pump.*

Weighing residues from evaporations. A bulky solution is first concentrated to a small volume in a beaker or dish, then transferred to a weighed capsule or crucible and evaporated to dryness on the water bath. A liquid held in a crucible is evaporated by laying the crucible as nearly horizontal as may be on a platinum triangle which rests on the ring of a retort-stand; a Bunsen burner is placed so that the flame is several inches below the edge of the crucible and turned as low as possible. Loss by spattering is guarded against by directing a fine jet of hot or cold air against the surface of the solution; evaporation on the water-bath is the safer plan, however.

A solution that tends to crystallize on the sides of the dish and creep over the edge by capillarity is best evaporated in a watch-glass resting on glass fragments contained in a larger watch-glass; any liquid passing over the edge of the smaller watch-glass is absorbed by the broken glass.

When the residue is to be dried at 100° or thereabouts, the most suitable vessel for the evaporation and weighing is a dish with a broad *flat* bottom rounded at its junction with the sides, leaving the residue in the form of a film uniformly thin and readily dried. Crystallizing dishes would be excellent except for the sharp corner; the best vessel for the purpose is made by cutting off a thin beaker about an inch from the bottom (by filing a notch in the glass and leading around a crack with the red hot end of a glass rod). The edge may be left sharp, or rounded in the Bunsen flame and a lip formed by pressing the plastic glass with a cold glass rod.

* Chem. News, 1889—2—249 and Journ. Amer. Chem. Socy. 1895—302.

If the residue is to be subsequently extracted by a volatile solvent, the final evaporation may be done in a small thin glass dish (schaelchen), afterward crushed and the fragments put in the tube of an extraction apparatus. Or a disk of tin-foil may be bent up to the form of a shallow dish and cut in pieces after the evaporation.

Solvent action of liquids. It has long been known that water and aqueous solutions dissolve appreciable amounts of powdered glass and porcelain, and to a less degree, corrode the surfaces of vessels containing them. The extent of this action in the case of water and solutions of the commoner reagents has been determined by several investigators. Comparison of their results shows marked discordances, explainable on the ground that glasses and glazes of unlike composition are unequally attacked by a liquid, and also that the technic of annealing probably influences the susceptibility of a given variety.*

In general, acids (except sulfuric and phosphoric) have but little effect, solutions of many salts considerable, and the alkalies and their carbonates an energetic action. It is said that the corrosive power is augmented by an increase in the temperature of the solutions, and that in presence of salts like sodium carbonate whose acid radicals form insoluble precipitates with the calcium of the glass, the action is greater the more concentrated the solution, while the reverse is true of those forming soluble calcium salts.

The following figures may serve as illustrations:—

Pure water evaporated in chemical glass flasks dissolved .014 grams per liter; boiled for 30 hours dissolved .0665 gram, in porcelain, one liter dissolved .0005 gram. By 30 hours boiling, water containing 11 per cent of hydrochloric acid dissolved .017 gram of glass and .005 gram of porcelain; with 7 per cent of ammonium chloride, .015 gram of glass, and .004 gram of porcelain; with 10 per cent of sodium carbonate, .450 gram of glass, and .024 gram of porcelain. Dilute sulfuric acid has twice the effect of water, and solutions of sodium and ammonium sulfates and phosphates act very strongly. Platinum is not affected by any of the above.

Cowper † heated 100 cc. of water and various aqueous solutions in glass vessels for six days to 100°. There was dissolved by pure water .009 gram of glass; by concentrated ammonia of .880 specific gravity, .008 gram; by hydrogen sulfide water, .011 gram; by ammonia water of .962 specific gravity, .035 gram; by concentrated solution of ammonium sulfide in water, .040 gram; and by dilute ammonium sulfide solution, .051 gram.

A highly resisting composition for glassware is that of an alkali-calcium silicate — the so-called Bohemian glass, which is inferior in this respect only to the Jena ware of Schott and Genossen, and the 'resistance glass' of Weber, made after special formulae.

For liquids of a low boiling point, as acetone, ether, carbon disulfide, either a temperature far below 100° is employed or the solution is allowed to evaporate spontaneously. On the other hand, those boiling above this temperature may be evaporated on the hot-plate or in a bath filled with glycerol or paraffin or a solution of some inorganic salt; if requiring a high temperature, as sulfuric acid, are heated directly over a burner, interposing a sheet of wire gauze to distribute the heat, and dropping scraps of platinum foil or the like into the liquid to prevent bumping.

Boiling with succussion. Some liquids are prone to boil with a succession of sudden bursts of vapor, frequently splashing out a part of the liquid or endangering the vessel. Especially is this true of liquids covering heavy and coherent precipitates; manganous ammonium phosphate, for example, must be constantly stirred while heating, even on the water bath. Bumping is more

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* Comey, Dict. of Solubilities, 169; Chem. News, 1891—1—62; Wiley, Agricultural Analysis, 1—347.

† Journ Chem. Socy. 1882—254

apt to occur on the hot plate or over a direct flame, and may be avoided by introducing a few fragments of glass or pumice or a spiral of platinum wire, from which the bubbles of vapor are quietly disengaged; or by passing a current of steam through the liquid if the introduction of water is not an objection. Methyl alcohol, one of the most troublesome on this score, boils quietly with a globule of sodium amalgam, and a solution of a caustic alkali with bits of zinc or aluminum, by reason of the constant slight evolution of hydrogen gas.

With emulsions and some solutions, such as milk, syrups and varnishes, a skin forms on the surface, retarding the evaporation or raising the temperature to a degree higher than is prudent in the presence of somewhat volatile oils, glycerol, etc., but if the liquid before evaporation is spread over a greater surface, as by imbibition in a porous solid, such as infusorial earth, blotting paper or purified wood sawdust, the water is quickly and completely dissipated at a low heat, and the residue, left in the form of thin films, is readily penetrable by a solvent. In some cases the liquid may be 'scaled' with advantage.

The foam arising from a liquid containing mucilaginous or saponaceous matter and liable to overflow the beaker or dish, may be caused to subside by the addition of a little alcohol, tannic acid, etc.* On boiling an aqueous solution covered with a layer of oil or liquid fatty acid, steam is apt to be suddenly and violently disengaged and throw out part of the liquid; here the best safeguard is the introduction of a current of steam through a narrow glass tube reaching to the bottom of the dish.

Protection from dust is essential to the correctness of a determination and is especially to be looked after in a laboratory occupied by several chemists. The usual device for protecting a beaker or dish is to cover it with a watch-glass, interposing a glass triangle to allow the escape of the steam. Or a Meyer's funnel may be used, a large glass funnel whose rim is curled inwardly to form a gutter which at one point opens into a short glass tube. The funnel is hung in an inverted position above the dish by the clamp of a retort-stand, and the water from the steam condensed on the interior of the funnel flows into the gutter and is led away through a rubber tube slipped over the glass tube.

DISTILLATION.

When a liquid is contained in a closed vessel in vacuo, evaporation takes place until the pressure (tension) of the vapor has risen to a certain point determined for any one liquid solely by the temperature; in other words for each temperature there is a specific vapor-pressure, assuming that some of the liquid remains unevaporated. Thus water at 100° has a tension of 760 mm. (measured at zero) of mercury, while at zero the tension is only 4.6 mm. The boiling point is also related to the vapor-pressure; as water boils at 100° under 760 mm. of mercury, and at zero when the pressure is reduced to 4.6 mm. If instead of a vacuum another gas or mixture of gases (as air) covers the liquid, evaporation takes place until the vapor at the surface of the liquid has reached a certain density also fixed by the nature of the vaporable liquid and the temperature.

Evaporating a liquid from a closed vessel and condensing the vapor is resorted to when the distillate is to be weighed or measured or further examined; to recover an expensive or scarce solvent for future use, or to avoid loading the air of the laboratory with disagreeable fumes. All apparatus for this pur-

* Journ. Anal. Chem. 1—116.

pose have three essential parts: a *still* for boiling the liquid, a *condenser* for liquefying the vapor, and a *receiver* for collecting the distillate.

The distilling vessel may be the venerable glass retort either plain or with a tubulure closed with a ground glass stopper or a cork carrying a thermometer. For liquids of high boiling point a porcelain retort is safer against cracking, and where fluorine or hydrofluoric acid is evolved, one of platinum or lead.

At present, however, a glass flask is more often used than the retort, closed by a cork carrying an exit tube connected with the condenser, or a side tube may project from the neck of the flask near the mouth. To prevent any of the contents of the flask from being carried over mechanically with the vapor, the safety tube shown in Fig. 170, or its equivalent, may be interposed in the exit tube.

The retort or flask is heated, according to the boiling point of the liquid, in a water or paraffin-bath, on the hot-plate, or directly over the flame of a large Bunsen. With aqueous liquids a current of steam may also be blown into the liquid, the moderate heat maintained avoiding the danger of decomposing certain organic bodies and also lessens the disagreeable and dangerous bumping from sudden evolution of vapor.* A copper or iron flask is safer than one of glass for liquids prone to boil with succussion.

It is always advisable to introduce in the distilling vessel some solid nuclei such as recently ignited pumice stone, scraps of platinum foil, zinc dust, etc., which not only promote regularity of boiling but largely increase the speed of the distillation.† Foaming of the liquid that may cause froth to pass into the condenser may be checked by the addition of a little alcohol, tannic acid, etc., or usually by previously heating the liquid to near the boiling point for some time in a beaker or dish.

The *condenser* is generally of glass, either the plain Liebig (Weigel) form, Fig. 62, or a modification. Cold water entering at the lower end of the condenser streams through the outer tube cooling the inner one which condenses the vapor entering it. To extend the surface of the inner tube exposed to the vapor, it may be coiled into a spiral or made up of a series of bulbs united by short narrow tubes. Since glass gives up traces of alkalies to steam, a block-tin, copper, or platinum worm, is substituted when distilling ammonia from aqueous solutions.

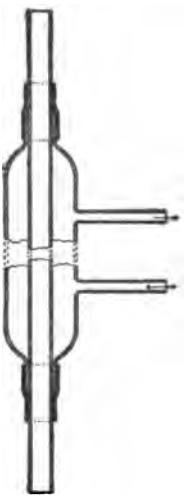


Fig. 62.

The current of cooling water should flow in the opposite direction to that of the vapor. Where the condenser is inverted or inclined so that the condensed vapor returns to the still, the rubber tube leading away the waste water should be higher at some point than the entrance tube.

For the condensation of a given volume of vapor per minute the size of the condenser to be used, i. e. the extent of the cooling surface exposed to the vapor, depends on (a) the efficiency of the condenser — the temperature of the cooling water, its rapidity of flow, the shape of the internal tube and its conductivity for heat; and (b), the constants of the vapor — the boiling point and latent and specific heats of the liquid; e. g., the conversion into vapor of one kilogram

* Chem. News 1897—1—279.
† *Idem*, 1888—1—244; 1892—1—226.

of water from zero requires 636 heat units, while the same weight of alcohol requires only 250, and of chloroform 81.8 heat units.

For liquids boiling at a temperature considerably above 100°, the condenser may be simply a long thin glass tube, the cooling effect of the air being sufficient to insure the liquefaction of the vapor.

The *receiver* is usually a glass flask of ample capacity. If the distillate is practically not volatile at the temperature of the air, the receiver may be a flask or cylinder loosely closed by a watch-glass, but with more volatile liquids it is connected to the condenser by a perforated cork, and another opening arranged with a capillary tube or a mercury seal to allow for expansion of the air within, yet prevent evaporation. Only with highly volatile distillates is it necessary to cool the receiver below the laboratory temperature.

Distillation in a current of some inert gas is resorted to when the liquid or vapor would be affected by contact with the air. For this purpose a tube connected to a gas generator is passed through the cork of a distilling flask, and another tube leads from the receiver to the open air. By these a slow stream of gas (generally carbon dioxide or hydrogen) is transmitted through the entire apparatus.

A distillation is conducted in vacuo when contact of the liquid or vapor with the air is not allowable on account of oxidation, where the liquid or some constituent is decomposed at the temperature of boiling under atmospheric pressure, or to promote the vaporization of some constituent. Here the connection of the condenser with the receiver is made air-tight and the apparatus is exhausted by a vacuum pump connected to a branch tube from the receiver.

The temperature of distillation of a commercial liquid is often a criterion of its purity; that the thermometer remains stationary or nearly so throughout the distillation indicates that no other volatile body of a higher or lower boiling point is present in any considerable proportion, and the range of variation in temperature in distilling a somewhat impure sample is a rough measure of the amount of a given impurity. However, some compounds suffer partial decomposition at the boiling point, the first part of the distillate differing from the last with consequent alteration in the temperature.

Besides the separation of a volatile constituent per se, distillation is largely applied for the removal of a gaseous or liquid constituent from an aqueous solution containing also non-volatile bodies. The distillate is a dilute aqueous solution or an emulsion of the volatile constituent. The proportion of water to be distilled in order to carry over all the volatile constituent depends not only on the proportion of the latter but on its nature and boiling point as well; in some cases the first small fraction of the distillate contains practically all the constituent, in others evaporation to dryness at 100° will not accomplish a complete separation, and repeated distillations with water are necessary.

Should the volatile constituent be an acid or alkali, originally free in the mixture or liberated by a stronger acid or base, the receiver may previous to the distillation be charged with a solution of an alkali or acid. If the latter is a standard volumetric solution in known volume, the determination may be at once proceeded with by a volumetric process. Advantages of this method are that the condenser need only be air cooled, and, provided the vapor is brought into intimate contact with the liquid in the receiver, there is no danger of any passing through uncondensed. Various other absorbents that react with the volatile compound may receive the distillate, such as an oxidizing reagent for a reducing gas and vice versa.

A method in frequent use is that of separating a volatile constituent *l* of a liquid *L* by distillation into a solid or liquid *L'* which reacts with *l* to form a non-volatile compound. In some cases the distillation is accelerated by the addition to *L* of a volatile liquid *V*. To avoid the use of the relatively large volume of *V* required, the distillation is several times repeated with only a moderate amount. A convenient apparatus for the purpose is shown in Fig. 62A, suspended in an inclined position from a support A as shown. The distillation of the mixture of *L* and *V* is made from the flask B through the condenser D into the receiver C charged with *L'*; then the apparatus is inclined in the opposite direction and *V* is distilled back into B, leaving the compound of *l* and *L'* remaining in C. The operation is repeated as often as necessary.

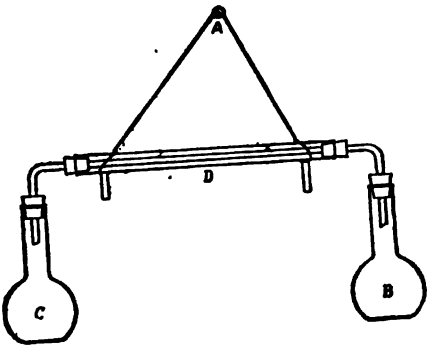


Fig. 62A.

Destructive distillation. When a dry organic substance is heated in a closed retort to a temperature above its point of decomposition, the products are various gases and vapors and usually a residue of tarry matter or pitch. Bituminous matter and animal or vegetable bodies are subjected to this operation as a check on a similar or identical manufacturing process.

Fractional distillation is applied to the separation of a mixture of a number of liquids each with a specific boiling point. The apparatus is, with one exception, practically identical with that for a simple distillation. Usually, though not necessarily, the constituent liquid having the lowest boiling point comes over first and passes through the condenser to the receiver. As the distillation progresses the thermometer rises, steadily if the boiling points of the various constituents are near together, but intermittently if they differ considerably, and at an increment of every few degrees the receiver is changed giving a graded series of distillates each of which may be further fractionated if desired.

For example, a distillation of 500 cubic centimeters of crude phenols from coal-tar oils gave Pattinson*: —

Water	230 Cc.	From 300° to coking	35 Cc.
Below 228° Cent.	15 Cc.	Pitch	72 Cc.
From 228° to 235°	27 Cc.	Loss	40 Cc.
From 235° to 250°	40 Cc.		
From 250° to 270°	26 Cc.	Total	500 Cc.
From 270° to 300°	15 Cc.		

In fractionating a series of volatile liquids in this way, the vapor arising at any moment is that of the fraction boiling at the current temperature of the still, accompanied by a portion of those boiling at a somewhat higher temperature. For a sharp separation, therefore, it is necessary to pass the vapors before entering the condenser, through a chamber heated only by the vapor itself and remaining consequently at a slightly lower temperature. In this chamber there condense and return to the still a small part of the vapor of the liquid vaporizing at the current boiling point, and also a large part of the vapors of the liquids of higher boiling points. The efficiency of this quasi-condenser determines the degree of individualization of the condensed products. It is known as the *dephlegmator* or *distilling tube*, and is essentially a wide glass tube, Fig. 63, clamped in a vertical position, connecting the still to

* Journ. Socy. Chem. Ind. 1882—499.

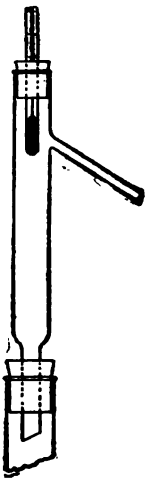
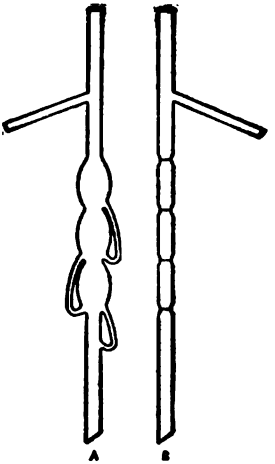


Fig. 63.

the condenser and cooled by the surrounding air. A thermometer passes through the cork closing the upper end, the bulb situated near the opening of the exit tube to show the temperature of the vapor entering the condenser.

To extend the surface exposed, in the Le Bel-Henninger tube, A, Fig. 64, are two or more external branches connecting the bulbs as shown; being narrow tubes and of thin glass, the vapor entering them readily condenses, the liquid flowing back into the large tube. Linmann's separating tube B is a bulbed tube obstructed by several diaphragms of platinum gauze in which the condensed liquid collects, washing the vapor as it rises through them. Hart's arrangement is a plain tube containing a number of glass funnels with stems bent to 180°. Various other forms are tubes filled with broken glass, pebbles, etc.



A B

Fig. 64.

The nearest to a complete partition is afforded by a reversed condenser over the still, the water heated to the proper temperature to condense all the vapors except that of the constituent of the lowest boiling point.

The efficiency of the dephlegmator is exemplified in the distillation of weak alcohol. By means of a long wide tube filled with glass beads, Hempel recovered alcohol of 95 per cent from that of 18 per cent; distillation from a flask directly would yield not over 90 per cent alcohol.

The following table* is a record of the progress of separation of a mixture of twenty-five grams each of benzene (boiling-point 80.4°) and toluol (b. p. 111°) during six distillations, A to F, of ten fractions each differing by 3° Cent. made in the following manner; after the first distillation A, the retort was cleaned and the first fraction of A introduced and distilled until the thermometer rose to 84°; the second fraction was then added to the residue of the first and distillation resumed until the thermometer again rose to 84°. The receiver, now containing the first fraction of B, was removed, an empty one substituted and distillation conducted up to 87°; the third fraction of A added and again distilled to 87° giving the second fraction of B. This routine was continued throughout.

VOLUMES OF THE DISTILLATES IN CUBIC CENTIMETERS.

°Cent.	81–84	84–87	87–90	90–93	93–96	96–99	99–102	102–105	105–108	108–111°
A.	1.0	10.0	14.5	8.0	6.0	5.5	2.5	3.5	3.5	3.5
B.	9.0	9.5	8.5	5.0	3.5	3.5	2.5	4.0	3.5	7.5
C.	17.0	7.0	4.5	3.5	3.0	2.0	2.5	2.5	2.5	10.5
D.	19.5	5.5	4.0	2.5	2.0	2.5	1.5	2.0	1.5	13.0
E.	21.5	4.5	3.0	1.5	2.0	1.5	1.5	1.5	1.5	14.5
F.	22.0	3.5	2.0	1.5	1.0	1.0	1.0	1.0	1.5	16.0

For fractional distillation in a vacuum, some means must be provided to prevent the entrance of air to the still and condenser during the operation of removing, emptying, and replacing the receiver. One apparatus for this purpose is shown in Fig. 65. The exit of the distilling tube A is joined to the inner tube of the condenser B, and this in turn with the funnel-tube C. Terminating C is a stopcock D fitted to the cork of the receiving flask E. Both C and E are connected by the tubes F and G to vacuum-pumps.

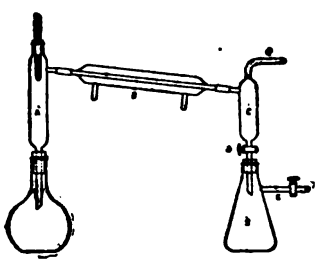


Fig. 65.

The stopcocks D and H being open, the pumps are started and the distillation begun. As soon as the first fraction has passed over, D and H

* Liebig's Annal. 224—259.

are closed and E removed and emptied, the second fraction meanwhile collecting in C. The receiver E is replaced and H opened, and when E becomes vacuous D is opened, the contents of C flowing down into E.

Distillation in a current of steam is often an advantage, as many organic bodies boiling in the air considerably above 100° distill in steam at but little above atmospheric pressure. From this it follows that the volume and boiling points of the several fractions distilled in steam may differ widely from those of an ordinary distillation. Superheated steam is necessary for bodies of a high boiling point.*

As regards the possibility of the separation of any two mixed liquids by fractional distillation, Regnault divides the pairs into three classes; those quite or almost immiscible, those which mix to a limited extent, and those mixing in all proportions.

1. With liquids totally insoluble in each other the vapor-pressure at any temperature is the sum of the vapor-pressures of the constituents at the same temperature, that is to say, the liquids evaporate independently of each other. Knowing the vapor-pressures and vapor-densities of the constituents, the boiling point can be calculated and also the weights of the two liquids in the distillate. If w is the weight of one constituent in the distillate, p its vapor-pressure and d its vapor-density, and w', p', and d', the corresponding values of the other constituent, then $w : w' :: d.\ p :: d'.\ p'$.

In all cases, the boiling point of the mixture is lower than that of either component and remains constant until nearly all of one has passed over, and the composition of the distillate remains constant until the quantity of one constituent of the mixture has become very small.

2. No fixed laws can be laid down for liquids mixing only to a limited extent, as they fall partly within the scope of class 1 and partly of class 3, but invariably the vapor pressure of the mixture is greater and the boiling point lower than that of either constituent.

3. Mixtures of the third class — those mutually dissolving in all proportions — behave quite differently according to the nature of the constituents. When the ratio of the members is at a certain numerical value, some pairs appear to unite to a compound of definite composition † which distills over unchanged, and where a different ratio exists, the vaporization of this compound is preceded or succeeded by that of the component which is in excess in the original mixture. For example, hydrochloric acid gas in water loses either gas or water, according to the strength of the mixture, until there remains a solution containing at 760 mm. barometer, about 20.2 per cent of the gas, which then distills as such, while with propyl alcohol and water, first the mixture of constant boiling point comes over, then the residue of alcohol or water as the case may be. It is evident that none of these mixtures can be separated by fractional distillation.

Other pairs of liquids have throughout the distillation a vapor-pressure and boiling point between those of the constituents, and whatever the relative proportions of the two liquids, no mixture of constant boiling point is had. These pairs may be parted more or less perfectly in proportion to (1) the divergence of their boiling points, and (2) the influence that the presence in different amounts of one component has on the boiling point of the other.

Sublimation. This principle is not often available since comparatively few solid bodies volatilize undecomposed within the range of temperature that

* Chem. News, 1899—1—200; 1898—1—25.

† Watts D'ct. of Chem. 4—137.

can be employed for this operation. A few alkaloids, benzoin and benzoic acid, camphor, chloral, iodine, iodoform, etc., may be sublimed with more or less success from less volatile bodies, but a loss by decomposition or oxidization or through imperfect condensation is almost unavoidable. The apparatus may be simply a light tared funnel inverted in an evaporating dish containing the substance heated on a sand bath; or a pair of closely fitting watch-glasses of equal size may be fixed edge to edge and the body sublimed from the under to the upper, interposing a perforated filter paper to prevent the sublimate from dropping back.

Bruehl's apparatus, Fig. 66,* is a platinum crucible A, surrounded by a copper box B, through which circulates cold water. Upon the box rests a light glass shade C. The sublimate collects partly on the upper plate of the box, and partly on the interior of the glass. The apparatus may also be arranged for sublimation in vacuo.

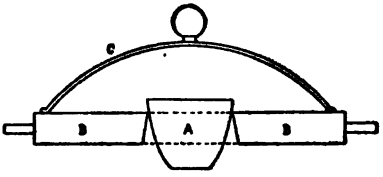


Fig. 66.

Another plan is to place the substance to be analyzed in a porcelain boat and push the boat to the center of a long wide glass tube laid horizontally in a combustion furnace (page 296). One end of the tube is connected with a gas generator or air blast, the other to a bulb tube containing water or solution of some reagent. The tube is heated to above the temperature of sublimation while a slow current of air or gas passes through the tube and bulbs. The volatile constituent sublimes and is partly condensed in the cooler part of the tube and partly in the liquid of the bulbs.

PRECIPITATION.

The conversion of a substance held in solution into an insoluble solid (or liquid) form is called precipitation, and may be considered as the continuous formation of a super-saturated solution which as continuously decomposes. Its purposes are to obtain a dissolved solid in a form suitable for weighing; as a means of separation from other bodies remaining in solution; or to remove matters from a solution whose presence would be prejudicial to subsequent operations.

Precipitation of an element or compound may be induced either by (1) so changing the condition or combination that it becomes insoluble; as antimony from an acid solution by hydrogen sulfide, copper by the electric current, or gelatin by formaldehyd; (2), reducing the solvency of the liquid by dilution, compounding with another liquid, etc.; as a resin in alcohol or barium sulfate in concentrated sulfuric acid thrown down by dilution with water, globulin precipitated from urine by carbon dioxide, or uric acid by hydrochloric acid; or (3), raising or lowering the temperature of the solution; as ferric hydrate precipitated on boiling a dilute neutral solution of a compound of iron with a weak acid radical, paraffin by cooling an alcoholic solution of petroleum to zero Cent., or the separation of the albumin of urine by boiling.

Precipitants may be either *general*, forming precipitates with each of several analogous bodies, or *specific*, affording a precipitate with but one or a few.

The best form in which to precipitate a body for a determination or separation — whether in the elementary state or as a particular one of several possible compounds all more or less insoluble — is to be decided by a number of considerations, aiming for a high degree of insolubility, rapidity of collection, ease of filtration and washing, stability on drying and ignition, and for compounds, a high molecular weight. It may also be an advantage when the pre-

* Berichte, 1899—238.

cipitate is to be weighed, if a specific precipitant can be used, avoiding the previous separation of other bodies in the solution.

The general rule that a body to be precipitated shall be held in a clear solution has some exceptions, as in the case of suspended and colloidal matter. Some insoluble bodies in fine powder are transformed to other insoluble compounds when long digested with a concentrated solution of a reagent, entering the solution for an inappreciable time. Thus, certain organic bodies form insoluble compounds with picric acid, and when one is digested in the solid form with a nearly saturated solution of the acid it is gradually replaced by its picric acid compound.

Solubility of precipitates. Since no precipitate is absolutely insoluble in the fluid from which it separates, in every precipitation it is important to know the degree of solubility in the liquid and the means to reduce it to a minimum.

The proper volume of the solution in which a precipitation is to take place depends on the bulk of the precipitate, the character and amount of other bodies present that are liable to impurify it, and especially on the solubility. For example, barium sulfate is so insoluble that a considerable dilution is not prejudicial to its complete separation, while with the far more soluble strontium sulfate, the fluid should be as concentrated as possible, even at the hazard of the occlusion of other compounds.

From a very dilute solution precipitation is slow and often less complete than the solubility coefficient would indicate. If evaporation is unallowable for any reason, a prompter and more complete separation is had by the addition to the solution of a known weight of the body to be precipitated in such a combination as is most convenient. A deduction is made from the weight of the total precipitate for the part inducted, with a correction for solubility.

It is sometimes desirable to conduct a precipitation in a dilute solution, yet for subsequent determinations to keep the filtrate small in volume. To save the time of evaporation the solution is divided into several equal parts; the first part is diluted to the proper concentration, precipitated and decanted or filtered; to the decanted liquid, with more of the precipitant if necessary, is slowly added the second part, this decanted, and so on with all the remaining parts. By this plan the necessary dilution is accomplished and the final filtrate not greatly increased in volume.

Where no precipitant is available for a sparingly soluble compound, the dilute solution may be concentrated to a small bulk whereupon the greater part of the compound precipitates or crystallizes out. What remains in solution is calculated from the volume of the concentrated solution, and the solubility of the compound therein, this found by an experiment on a solution similar in composition to the one in hand.

The solubility of a precipitate is sometimes lessened by the admixture of another liquid in the solution; thus, calcium malate is less soluble in a dilute alcoholic than in an aqueous solution; ether-alcohol dissolves less of certain organic compounds than alcohol alone; etc.

As a rule, the solubility of a complex precipitate is lowered by the presence of a soluble compound of one of its radicals; thus, one part of lead chloride dissolves in 120 parts of water and in 437 parts of a five per cent solution of sodium chloride. But in some cases should the concentration exceed a certain proportion the solubility is increased; as lead chloride dissolves in 129 parts of a concentrated solution of sodium chloride — nearly as freely as in water. On the other hand it is sometimes advantageous to fully saturate the solution with the precipitant or a similar salt.

An aqueous solution previous to precipitation may be saturated with the same compound as the precipitate — if a solution of potassium tartrate be compounded with a slight excess of acetic acid, one-half of the potassium is abstracted by

the acid — $K_2C_4H_4O_6$ (potassium tartrate) + $HC_2H_3O_2$ = $KHC_4H_4O_6$ (potassium bitartrate) + $KC_2H_3O_2$ (potassium acetate) — and the potassium bitartrate precipitates; but only completely, since it is somewhat soluble in water, if the solution before acidification was saturated with potassium bitartrate by shaking with some of the solid salt and filtering from the excess.

Many organic compounds impede or totally prevent the precipitation of certain bases by alkalies, alkali phosophates, etc.* Ferric citrate or tartrate is not clouded by ammonia, and the presence of gallic acid, sugar, glycerol, and the like have a similar effect, so that it is safer to destroy or eliminate organic matter from a solution before precipitation by these reagents, or to choose another precipitant.

It may happen that two bodies are present in a solution both forming precipitates with a given reagent and, according to the usual procedure, must be separated before the reagent may be applied for a determination. But a separation can be omitted if the precipitates differ greatly in solubility and only the body forming the more insoluble precipitate is to be determined (as in an assay), by making the precipitant a saturated solution of the more soluble precipitate. Thus, however great may be the proportion of lead nitrate mixed with silver nitrate, only silver chloride falls when the precipitant is a solution of lead chloride; similarly only quinine iodosulfate is precipitated by a solution of chinoidine iodosulfate, from a solution containing quinine and chinoidine.

When a precipitation is to take place in a strictly neutral solution, a dilute acid and alkali are alternately poured in with the addition of some indicator until a drop of either reverses the reaction; or when it is undesirable to introduce any traces of organic matter, the reversal is observed by spotting the solution on litmus or turmeric test-paper. A much easier way to obtain neutrality is first to either slightly acidify the solution if it is alkaline, or nearly saturate any free acid by an alkali, and then stir in an excess of some solid reagent that is insoluble in water but readily soluble in the acid, and whose presence in the solution and precipitate is unobjectionable; the hydrate or oxide of the base of the precipitant is often suitable.

Thus in precipitating tungstic acid; first, any free mineral acid in the solution is neutralized by stirring in some mercuric oxide, then a solution of mercurous nitrate is added, and the precipitate of mercurous tungstate, mixed with the excess of the mercuric oxide is filtered; on ignition *all* the mercury is expelled leaving pure tungstic acid ready for weighing. The same effect is obtained without the use of an insoluble base by adding to the slightly acid solution a large excess of the precipitant followed by enough alkali to more than neutralize the free acid, yet not sufficient to combine with all of the excess of the precipitant.

Some metals are precipitated by hydrogen sulfide only when in combination with a weak acid such as acetic, and to convert the metal from a combination with a strong acid to an acetate it is customary to add an excess of an alkali acetate. Thus, a solution of zinc chloride containing free hydrochloric acid on the addition of sodium acetate —

$ZnCl_2$ (zinc chloride) + $2NaC_2H_3O_2$ (sodium acetate) = $Zn(C_2H_3O_2)_2$(zinc acetate) + 2NaCl (sodium chloride).

HCl (hydrochloric acid) + $NaC_2H_3O_2$ = NaCl + $HC_2H_3O_2$ (acetic acid).

It is said that the excess of the alkali salt favors the precipitation by lessening the ionization and consequently weakening the solvent power of the organic acid set free by the excess of the mineral acid and the hydrogen sulfide.

When precipitating a body from a complex solution it must be learned

* Ostwald-McGowan, Foundations of Anal. Chem. 138.

whether the associates are of a nature and present in a quantity likely to seriously impurify the precipitate by co-precipitation or occlusion; where this is probable the safest plan is to separate the body before precipitation. There are cases, however, when simply changing the combination of the impurities to other radicals will insure their remaining entirely in solution. For example, in the precipitation of sulfuric acid by barium chloride in presence of ferric chloride, by changing the ferric chloride to ferric oxalate any contamination of the barium sulfate with iron will be prevented.

The complete segregation of a precipitate from the solution in which it is formed may take place almost instantaneously or not until after a more or less protracted repose, conforming to the nature of the precipitate and the conditions under which it is formed. Brisk agitation of the liquid after the addition of the precipitant hastens deposition, a vigorous stirring or shaking in a stoppered flask or passing a rapid stream of air for ten minutes is as effectual as an hour's repose. The device for agitating the liquid shown in Fig. 36 is of general service.*

Heating the liquid greatly favors the collection and should be done whenever allowable. Boiling has a still more pronounced effect in causing a precipitate to clot and settle well, and is necessary in some cases for the expulsion of a volatile compound in the excess of which the precipitate is somewhat soluble.

The precipitant may be either a liquid, gas or solid, but for several reasons an aqueous solution is generally to be preferred, and as a rule a gas or solid is introduced into the solution of the body to be precipitated only when it is insoluble or sparingly soluble in water or other available solvent. Crystalline salts are dissolved in water to a convenient strength, alone or compounded with other chemicals if required for solution or preservation.

A soluble precipitant is introduced in the solid form with the purpose of saturating the solution to insure the entire precipitation of certain organic compounds; to promote the flocculation of a finely divided or slimy precipitate; or in cases where precipitation must take place from a highly concentrated solution and even the dilution caused by a solution of the reagent is detrimental.

An insoluble reagent is made the precipitant when it is desirable that no extraneous body be brought into the solution beyond an equivalent of the precipitant. Here either the precipitation may be only an apparent mechanical absorption, as where a coloring matter is withdrawn from solution by oxycellulose, or a proteid by copper hydroxide; or it may be the result of a distinct chemical reaction, as when a ferrocyanide is decomposed to form mercuric cyanide and iron oxide on boiling with water and mercuric oxide.

Even an already formed precipitate may be entirely changed to another insoluble compound by suspension in water or other liquid, adding a suitable reagent and heating the mixture.

Frequently the insoluble precipitant is an oxide or carbonate of a metal that reacts in a similar way to a soluble salt of the metal, as when silver carbonate is substituted for silver nitrate for the removal of hydrogen sulfide from a solution; any free acid in the solution is neutralized at the same time. This

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* Chem. News, 1892—1—143; Journ. Anal. Chem. 4—57; Wiley, Agricultural Anal. 2—144; Chem. Centralb. 1896—68.

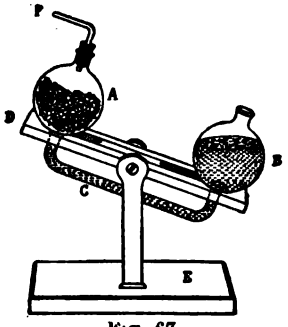

Fig. 67.

plan is more suitable for a separation than for a determination; for the latter the necessary excess of the precipitant must be entirely volatile at a considerably lower heat than will affect the precipitate (e. g., mercuric oxide), or be otherwise removable in order that the precipitate can be weighed.

When a gas is so sparingly soluble in water that it must be carried into a solution in the gaseous form to avoid great dilution, it is best furnished from a constant generator. Of these there are three types and many modifications. All are so contrived that the generation of gas may be initiated and terminated at pleasure, preventing waste and the nuisance of gas escaping into the laboratory.*

As arranged for the production of hydrogen sulfide the three typical generators are—

1. Von Babo's, Fig. 67, consists of two heavy glass globes A and B united by the tube C, and mounted in a frame D, pivoted in the center to the wooden stand E, so that they may be fixed at the angle shown, or inclined in the reverse position bringing B higher than A. A is filled with lumps of fused iron sulfide or barium sulfide, the opening into C being loosely plugged with cotton. Dilute muriatic acid is poured into B until filled, the gas evolved passing out at F, through a wash-bottle containing water, to the solution to be precipitated; when this is saturated, the frame D is reversed, the acid running back into B.

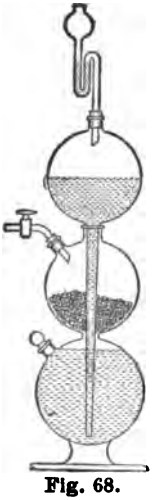
Fig. 68.

2. Kipp's, Fig. 68,† has three glass globes, the upper one A, terminating in the tube D, fitted to B by a ground socket. B holds lumps of iron sulfide, and has a tubulure near the top from which passes the exit tube. A is filled with dilute acid, and when the stop-cock C is opened, the acid rising into B generates the gas. To discontinue the flow, C is closed and the pressure of the gas accumulating in B forces the acid from thence back into E and A.

3. Schranche's, Fig. 69.‡ A long glass jar A contains the iron sulfide, and the bulb B dilute hydrochloric acid; this after percolating through A is so far weakened and impregnated with ferrous chloride as to be of no further use, and is allowed to flow away by C into a waste-pipe.

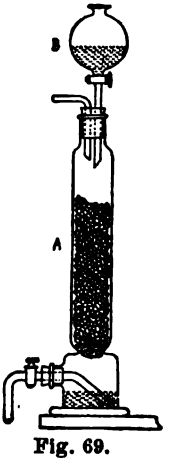

Fig. 69.

Other gases may be generated in the above described apparatus. Substituting zinc for iron sulfide gives hydrogen; calcium hypochlorite, chlorine; maganese and barium peroxides, oxygen; calcium carbide and water, acetylene; etc. A steady current of hydrochloric acid gas is furnished when the strongest commercial acid is dropped from a funnel tube into hot, fairly concentrated sulfuric acid; and of ammonia by gently heating the strongest liquor ammoniae and passing the ammonia gas through a desiccating medium to absorb aqueous vapor.

Where an aqueous or other solution is to be precipitated by a gas without being reduced in volume through the solvent being carried off as vapor, the gas is previously saturated with the solvent by passing through a wash-bottle containing it.

Beakers and Erlenmyer flasks serve well for precipitations as the completion of the reaction and the settling of the precipitate can be plainly seen, but flasks

* Chem. News, 1888—1—213 and 1893—2—52; Journ. Amer. Chem. Socy. 1898—344.

† Journ. Amer. Chem. Socy. 1898—344.

‡ *Idem*, 1894—868 and 1897—818.

are not suited to those whose particles become firmly attached to the glass and are difficult to remove; this objection does not hold when the precipitate is to be redissolved for further treatment. On account of the solubility of glass in free alkalies, their carbonates and some other salts, porcelain, platinum or silver dishes are more suitable for use with these reagents.

Precipitates of compounds containing silver must be protected from actinic light which causes decomposition with loss of weight. If precipitation and filtration are done by gaslight or very subdued daylight, and the precipitate allowed to settle and dry after filtration in a dark place, the decomposition will be only superficial and may be neglected. Beakers, flasks and watch-glasses of amber non-actinic glass are on the market.

A solution of a base oxidized by the air is manipulated in a closed flask in a current of some non-oxidizing gas such as carbon dioxide or hydrogen. The precipitant is introduced by a syphon through a funnel tube with a stop-cock, and the liquid drawn off after the precipitate settles. But on account of the complexity of the apparatus some other method of analysis is generally chosen.

Amount of precipitant. A slight excess is always added to insure that a sufficiency has been used. Frequently this tends also to decrease the solubility of the precipitate — in a few instances a large excess is necessary for this purpose or to produce some physical or chemical change in the precipitate. Yet in other cases any excess whatever is objectionable and must be removed before filtration.

A common error of beginners is that of using a great excess. This is to be avoided (unless specially directed), as it augments the necessary washing of the precipitate and all subsequent ones to an undesirable extent, and in some cases may cause decomposition of the precipitate. Ordinarily some indication is given at the point when sufficient has been introduced, such as the cessation of clouding or a reversal of the reaction; when such evidence is doubtful, the amount of reagent required for a given precipitation can be calculated from the equation narrating the reaction, and a measured volume used.

Solutions too dilute for convenient handling, or when the compound to be thrown down is not highly insoluble, are concentrated by evaporation to a small bulk with precautions to prevent loss when dealing with bodies volatile at steam heat. After noting that the liquid has the reaction directed by the method followed, it is heated to boiling (unless the precipitation is to take place in the cold) and from a graduated cylinder is run in as much of the solution of the reagent as it is presumed will suffice. An approximation to the volume needed can be learned by a calculation from the combining proportions. If an alkali or alkali carbonate is the precipitant, a strip of red litmus paper will show when the reaction becomes alkaline; sometimes a visible alteration in the liquid or precipitate will indicate an excess.

As a rule the precipitant is best added slowly, even by drops, and with constant stirring, for the reason that less of the precipitant may be occluded or mechanically inclosed by the precipitate than if added at once in full amount; again the transformation of an amorphous to a crystalline (more easily filtered) form is favored by contact with already formed crystals. Exceptions to the rule are where only by a sudden admixture does the precipitate form in a physical condition suitable for decantation or filtration.

In some determinations the solution to be precipitated is slowly added to the precipitant, as here the latter remains in excess throughout the formation of the precipitate. Certain precipitates are only to be obtained of a definite composition by proceeding in this way.

After mixing well, the precipitate is allowed to subside and a few drops of

the reagent run down the side of the beaker into the supernatant liquid. If no cloud is formed, the whole is stirred vigorously for a few minutes and digested for the prescribed time before filtering. When a precipitate is slow to settle, the addition of a few drops of chloroform and boiling, or intermixing a heavy powder like barium sulfate may hasten its deposition; minute amounts of a precipitate too finely divided to be caught by a filter may be entangled by stirring in some insoluble body of a flocculent or gelatinous nature.

After allowing the liquid to stand, in the cold or heated as directed, until the precipitate has subsided, the liquid is ready for the process of filtration.

SEPARATION.

When two or more elements or compounds are to be determined in a substance the usual procedure is to part them by a suitable process and determine each individually. Every method of separation should comply with two conditions, namely, that the separation be complete within reasonable limits, and that the reagents introduced into the solution shall not interfere with further operations, or if so, can easily be removed. It is also an advantage if the separated compound is in the solid form in a combination suitable for weighing.

Methods of separation based on the following principles are employed as conditions indicate. Some are entirely physical in nature, while others are preceded by a chemical reaction. Unlike qualitative analysis, the methods as a rule separate not one group from another but each constituent in turn.

In some instances, as where a substance is made up of several analogues they may be separated by the application of one principle only; as the organic constituents of the mineral asphaltum dissolved out successively by ether, benzene and carbon disulfide, or the hydrocarbons of crude petroleum isolated by fractional distillation. Usually, however, more than one must be resorted to, especially for complex mixtures.

1. Mechanically. A light powder may be floated from a heavier by a liquid of intermediate density, as gypsum from barite by a solution of mercuric potassium iodide, their respective specific gravities being 2.2, 4.5, and 3.0. Silt, dust, clay and sand of different degrees of fineness and gravity are washed one from another by a stream of water in a special elutriating apparatus. From flour, cold water washes the light pulverulent granules of starch out of the cohesive gluten.

Two immiscible liquids of different specific gravities can generally be made to stratify so that one may be drawn off or filtered from the other; as ether after collecting an oil emulsified with water. The bibulous capacity of a porous solid (bone-ash) is employed in the cupellation of lead alloys. Particles of iron, nickel and magnetic minerals may be drawn from a powder by a magnet or electro-magnet; and the attraction or repulsion of electrified particles by static electricity has been proposed for their separation.

From a solution a solid may withdraw by adsorption certain forms of dissolved matter nearly or quite completely. The well-known decolorizing power of bone-black and Fullers earth are examples; gelatin, amorphous silica, ferric oxide, alumina, magnesium carbonate, and vegetable fibre fix certain organic bodies, and for an assay of an impure dyestuff the first step may be the extraction of the dye from its solution by raw silk.*

Various other mechanical processes are employed for special material.

2. Solubility. The bodies to be separated, solid, liquid, or gaseous, may be

* Chem. News, 1894—1—33 and 43.

such that the application of a solvent will extract one from the others directly. Thus, nitre is lixiviated from gunpowder by water; silk from wool by warm hydrochloric acid; strychnia extracted from nux vomica by chloroform; the acid radical of xanthin sulfate washed from the xanthin by water; cinchonine, cinchonidine, etc., from quinine by washing with a saturated solution of quinine; copper from a finely powdered alloy of copper and silver by a solution of zinc chloride; an oil collected from an emulsion with water by ether; or ethylene absorbed by bromine from a mixture of gases.

Before applying the solvent some preliminary operation on the mixture may be necessary to render one or more of the constituents soluble or insoluble as the case may be, and may be either mechanical or chemical. Change in valence, reduction or oxidation, hydrolysis, saponification, polymerization, etc., are the most usual chemical alterations. A semi-organic compound may be decomposed by an inorganic acid or base and the liberated organic radical extracted by a suitable solvent from the solution; an example, where both the radicals are insoluble in water, is that of napthol-yellow, the calcium salt of dinitronapthol; on treatment with sulfuric acid there precipitate calcium sulfate and dinitronapthol, the latter soluble in ether.

Some metallic sulfides are decomposed on treatment with a reagent evolving nascent hydrogen, the constituents separating. Thus, bornite in contact with zinc and hydrochloric acid is decomposed to a residue of metallic copper, a solution of ferrous chloride, and gaseous hydrogen sulfide ($Cu_3FeS_3 + 2HCl + 2H_2 = 3Cu + FeCl_2 + 3H_2S$).

An extension of the principle of separation by a solvent is in the treatment of a mixture of bodies by a succession of different solvents each removing one constituent, and it is often possible to resolve a complex mixture into groups by this process, each group to be further subdivided by other methods. Thus, in the analysis of a detonator, mercury fulminate is extracted from antimony sulfide and potassium chlorate by acetone saturated with ammonia, then potassium chlorate from antimony sulfide by water; in plant analysis, solvents are applied in about the following order: chloroform, methylated spirit, cold water, dilute sulfuric acid, dilute sodium hydrate, bromine with ammonia, and special solvents like cupric oxide in ammonia, etc.

A mixture of several analogous bodies may be roughly divided by fractional solution — treating the powder with successive small portions of one solvent. The most easily soluble of the constituents is withdrawn by the first portion, the others in the order of their solubilities. The operation is best performed in a small percolator, allowing each portion of the solvent to digest with the powder for some time before tapping out. It will readily be seen that neither the principle nor practice of this method is compatible with more than crude results, except in the case of binary mixtures whose composition is approximately known and for which a correction for solubility can be predetermined and applied. For although a constituent be practically insoluble in the pure solvent it may dissolve much more freely in the solution of a more soluble constituent especially when concentrated, and the process does not admit of the usual precaution of employing an adequate amount of solvent to insure a dilute solution.

Extraction of the several constituents of a mixture of analogous bodies by means of a solvent applied at different temperatures has been proposed for the separation of the various tannins from tan-wares, etc.

In a mixture of two salts both soluble in water or other liquid, one may be insoluble in a concentrated solution of the other, and in separating them by lixiviation the volume of the solvent is kept as small as possible. If one of the salts is deliquescent, the mixture can be placed in a paper filter and exposed for some days to a damp atmosphere, when

the deliquescent salt will have liquefied and passed through the paper; thus caesium tartrate from rubidium tartrate.

An approximate determination of the proportions of two bodies admixed, the one A much more soluble in a given liquid than the other B, may be made in the following way: the mixture is treated with a measured volume of the solvent, the solution decanted, evaporated to dryness, and the residue weighed; from the weight is deducted the amount of B soluble in the volume of solvent used. Thus if one gram of a mixture of phenacetin and acetaniliid be stirred in 200 cubic centimeters of cold water, all the acetaniliid goes into solution together with .180 gram of phenacetin.

A variation of the above is as follows: after weighing the residue from evaporation the original residue is again treated as before, and this process continued until successive weights of the residues show by their again becoming equal that the residue from the last solution consists entirely of B. If the solubility-coefficient of B in the solvent is exactly known, the calculation is simple: let r, r', r'' .... be the weights of the residues; $v, v,'$ v''....., the volumes of solvent; and s, the volume of solvent dissolving one gram of B; then the weight of the constituent A is $r + r' + r'' + .. - \frac{v + v' + v'' + ...}{s}$. The formula assumes that the rate of solubility of B is independent of the presence of A in the solution and vice versa; if this is not the case, a correction must be found by experiment and applied.

Another method, where the proportions of the constituents and their solubilities are approximately known, is to treat the weighed mixture with a volume of solvent sufficient to dissolve all of A but not all of B. The solution is decanted and evaporated and the residue weighed; this residue is then treated with a somewhat smaller volume of solvent though still sufficient to dissolve all of A; the solution decanted, evaporated, and the residue weighed. The operation may be again repeated.

Let v and v' be the respective volumes of the solvent; and r and r' the weights of the residues. Then $r - r'$ is the weight of B soluble in $v - v'$; and the weight of B dissolving in one cubic centimeter of a solution of A is $\frac{r - r'}{v - v'}$

Also $\frac{v\,(r - r')}{v - v'}$ is the weight of B in r. Hence the weight of A in the first extraction is $r - \frac{v\,(r - r')}{v - v'}$.

Certain bodies dissolve in a mixture of two liquids to an extent governed by their proportions in the mixture. At times this property affords an easy way of determining approximately the purity of a commercial article. The test may be applied by dissolving the substance in a measured volume of one of the liquids and slowly adding measured volumes of the other until permanent opalescence or turbidity appears. An example is the dissolving of an essential oil in absolute alcohol and adding water to turbidity.

The process of electro-dissolution is employed in a few cases, as in the analysis of an impure commercial metal. On dissolving in hydrochloric acid certain constituents are exposed to the action of the nascent hydrogen, evolved by the solution of the metal in the acid, and enter into combination with it and pass off as gases. But if the metal be made the anode and a sheet of platinum the cathode of an electric circuit by connection with a battery of suitable strength, no free hydrogen appears, and these constituents remain suspended in the solution in the free state or combine with the acid and enter the solution.*

In all cases, before applying a solvent for the extraction of a constituent of a complex mixture, it must be learned whether any of the following effects supervene so far as to impair the separation: (1), a chemical action between the solvent and constituent to be extracted; (2), a solvent action of the solution of the soluble constituent on one or more of the insoluble constituents;

* Chem. News, 1887—1—62.

(3), a chemical reaction between the solution of the soluble constituent and one of those that are insoluble; (4), a reaction between the various insoluble constituents brought about by contact with the solvent; and (5), action of the oxygen or carbon dioxide of the air, common impurities of the solvent, etc.

Extraction. When a solid is brought in contact with two repellant liquids, being fairly soluble in each, it may dissolve in either according to circumstances; but immediately a translation begins, terminated when it is divided between the liquids in a ratio determined by their volumes and a specific coefficient.

"When* the molecular complexity of the dissolved substance is the same in both solvents it so distributes itself between them that at any given temperature there is a definite ratio between the concentration of the two solutions when equilibrium is attained, the ratio being independent of the amounts of substance and solvents originally taken. Thus iodine when shaken up with carbon tetrachloride and water is shared by these solvents in such a way that the concentration of the aqueous solution produced is to that of the carbon tetrachloride solution as 1 to 85, that being approximately the ratio of the solubilities of iodine in the two solvents at 25°, the temperature of the experiment. When the molecular complexity of the dissolved substance is not identical in the two solvents, there is no constant ratio of distribution, the ratio of the concentrations varying with the original quantities present. There is, however, in such cases a somewhat more complex function which takes the place of the simple distribution ratio. If the molecular weight of the substance in one solvent is n times as great as its molecular weight in the other solvent, then when equilibrium is attained, the nth root of the concentration in the first solvent will bear a constant ratio to the concentration in the second solvent."

Thus, if butter-fat be agitated with a mixture of alcohol and carbon disulfide and the liquids allowed to separate, the lower stratum of carbon disulfide will contain the fat, and the upper alcoholic stratum the artificial coloring matter, water, salt, etc.

The principle is applied much more frequently for the extraction of a solid or liquid already in solution than for the direct solution of a solid or liquid in the mixture of two liquids.

For example, let it be required to recover an alkaloid from its solution in water. The solution is shaken up with a moderate quantity of benzin, then allowed to stand until the liquids have separated. The benzin is decanted and the 'shaking out' repeated with fresh benzin. After a few repetitions practically all of the alkaloid will have passed into the several volumes of benzin, the greater part into the first portion, and the least in the last.

For separating an alkaloid from other bases a peculiar property is availed, namely that many free alkaloids are comparatively insoluble in water but freely soluble in ether, benzene or chloroform; while on the other hand, their salts are insoluble in these liquids, but soluble in water. So if an impure aqueous solution be acidified and mixed with chloroform and the liquids separated, the chloroformic solution contains such of the impurities as dissolve in it, while the salt of the alkaloid is retained in the aqueous solution. The latter is made alkaline and again shaken with chloroform; the alkaloid, now in the free state, is taken up, leaving the remainder of the impurities in the aqueous solution. Usually

* Journ. Chem. Socy. 1896—1334.

these separations have to be repeated to isolate the alkaloid in a fairly pure state and nearly completely.

By extraction with suitable solvents applied to acid, neutral, and alkaline solutions, the various organic constituents of a mixture may be successively removed. Thus, Husemann divides the ptomaines into five groups: (1), extracted from an acid solution by ether; (2), from an alkaline solution by ether, (3) from an alkaline solution by chloroform; (4), from an alkaline solution by amyl alcohol; (5), not extracted by any of these solvents, but soluble in water.

Up to the present time, the application of this principle has been mainly restricted to organic bodies. A few inorganic compounds in aqueous solution may be separated by organic solvents, such as the sulfocyanides of cobalt and nickel by a mixture of ether and amyl alcohol, and ferric from manganous nitrate by ether. But other and more convenient and less costly methods are generally at hand.

In applying a succession of organic solvents, regard must be had in exact analyses to their solubilities in water or aqueous solutions. While few dissolve to any great extent, yet enough of one may enter the solution to modify the solvent action of the succeeding one, so that it is advisable to remove the former as completely as may be before applying the latter. By beginning the sequence with gasoline which is practically insoluble in water, what dissolves of the next solvent, such as ether or chloroform, may be removed from the solution by shaking out with gasoline; the latter after separation should be entirely volatile, but if there be any residue on evaporation, it is returned to the aqueous solution.

When a liquid a passes from one solvent b to another c the volume of c becomes approximately $c + a$, while that of b becomes $b - a$. An application of this fact is for the determination of small amounts of amyl alcohol in commercial spirits. A certain volume of the spirit, brought to a definite gravity, is shaken up with an exactly measured volume of chloroform. When the chloroform has separated, the increase represents the volume of amyl alcohol. The process is only approximate at best, the chief error being the contraction of $a + c$, and requires strict attention to details of manipulation.

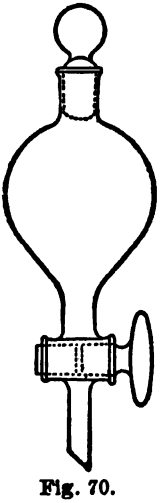

Fig. 70.

An extraction is usually made in a separatory funnel, Fig. 70, of a size adapted to the mixture. After stoppering the funnel the two liquids are mixed by shaking (less or more violently according to the tendency of the liquids to unite to an emulsion). After standing until the liquids have separated, the stopper is removed and the heavier drawn out through the tap.

An apparatus designed for the extraction of an aqueous solution or an emulsion with water is shown in Fig. 71. The emulsion is poured into the funnel A partly filling B and C, and the ether or other light solvent into the flask D. After capping A with a condenser E, the flask is heated and the vapor rising through F and G into E, is there condensed, and dropping into C displaces the emulsion. From C it ascends in drops through B dissolving out the oil, and when B is filled, the solution finally runs over through F into D.

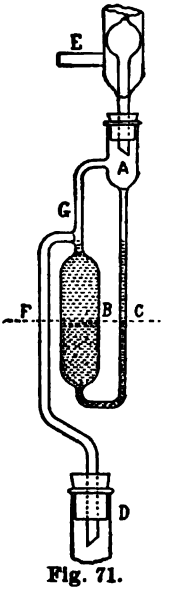

Fig. 71.

The above will not answer for a solvent heavier than water, like chloroform or carbon disulfide, and for these, Schiebler's apparatus is arranged as shown in Fig. 72. The stem of the funnel A is bent to enter the flask C, while the neck of A holds a condenser B and a tube D passing to C. The emulsion is contained in A and the solvent in C, and as the vapors are condensed in B the resulting liquid falls through the emulsion and returns through the stem to C.

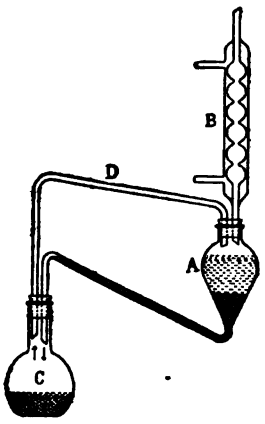

Fig. 72.

Many bodies are more easily extractable if the solution be saturated with some inorganic salt, such as sodium chloride, insoluble in the inorganic solvent. According to Ostwald, only the non-ionized portion of a body passes from one solvent to another, and the original solution should be as concentrated as circumstances will permit that the minimum of ionization be attained, and when dealing with an acid of moderate strength there should be added a stronger (mineral) acid, and with a moderately strong base, one of the alkalies.

The rate of distribution for non-ionized solids or liquids between water and an immiscible organic solvent (e. g., for an aqueous solution agitated with benzin), may be expressed as

$$\frac{\text{Weight passing into benzin}}{\text{Volume of benzin}} : \frac{\text{weight remaining in water}}{\text{volume of water}} :: 1 : K.$$

K being the distribution coefficient. This may be written

Volume of benzin : $K \times$ volume of water : : weight in benzin : weight in water.

Since K and the volume of water are constant, the ratio of the amount of the solid entering the benzin to that remaining in the water increases directly with the volume of benzin. It is evident that a single treatment will extract only so much of the solid as corresponds to the respective rates of solubility in water and the organic solvent, and this ratio determines the number of times the agitation must be repeated with fresh portions of the solvent to ultimately arrive at a reasonably complete separation — traces (or more) of the solid will inevitably be retained in the original solution.

If S represents the original weight of the solid in the volume V of the aqueous solution; V', the volume of the organic solvent; K, the distribution coefficient; S', the weight of the solid remaining in the aqueous solution, and $S - S'$, the weight passing into the organic solvent; then for the first extraction,

$$V' : KV :: S - S' : S', \text{ whence } S - S' = \frac{SV'}{V' + KV} \text{ and } S' = \frac{KVS}{V' + KV}$$

For the second extraction with a (usually smaller) volume V'' of the organic solvent the volume of aqueous solution being practically the same as before,

$$S - S' = \frac{S'V''}{V'' + KV} \text{ and } S'' = \frac{KVS'}{V'' + KV},$$

and so on.

If the organic solvent is soluble to any extent in the aqueous solution, the solvent power of the latter saturated with the former must be considered. Ethyl ether is the only solvent in common use that mixes with water to a marked degree.

Mixed gases may be passed through a solution of a reagent combining with and retaining one or more of the constituents, while the others pass through unabsorbed. Thus, when commercial zinc is dissolved in a non-oxidizing acid, any arsenic contained is converted into arsine and is carried off with the

hydrogen evolved by the solution of the metal; on conducting the mixed gases into a solution of a silver salt the arsenic is retained in the solution as arsenious oxide, through the decomposition of an equivalent of the silver salt.

Several of the constituent gases of a mixture may be absorbed seriatim in a train of absorption tubes, each filled with the special reagent to retain one of the members (page 146).

3. Heat. On heating a solid to the required temperature any volatile constituent is vaporized; it may be condensed on a cold surface, as iodine sublimed from earthly impurities, or absorbed in a liquid or porous solid and its weight found by the increase; or the absorbent is further treated to obtain the constituent in a form suitable for weighing. Thus on ignition of zinc carbonate the carbon dioxide may be passed through a solution of barium hydrate contained in a suitable vessel, the increase in weight of the latter equaling that of the carbon dioxide; or the precipitated barium carbonate may be filtered off and weighed, and the weight of the carbon dioxide calculated therefrom.

More usually the volatile element or compound is allowed to escape, its weight equaling that lost by the substance; thus, silver is volatilized from gold by intensely heating their alloy. Combined water and unimportant amounts of organic matter in minerals and ores are often determined in this way, the results set down as "loss on ignition" or "volatile at a red heat," it having been ascertained that the residue is of such a composition as not to be altered in weight by oxidation, reduction, or through inter-reactions initiated at a high temperature.

The metals of certain alloys can be separated by heating the powder in a current of some gas which combines with one metal to form a volatile compound while the other metals are either unaffected or the products are not volatile at the maximum temperature employed. Dry chlorine and gaseous hydrochloric acids are the usual reagents for the purpose, as many metallic chlorides are vaporable at or below a red heat. Many alloys that are insoluble in all acids are readily decomposed by ignition in chlorine, the volatile chlorides passing over, and the fixed chlorides remaining in a crystalline form; metallic oxides are previously reduced to the metallic state by heating in a current of hydrogen or formic acid vapor. Native sulfides can be opened up by heating in dry air loaded with the vapors of bromine,* and some alloys converted to volatile or fixed sulfides by ignition in the vapor of sulfur.†

The vapor of a halogen traversing a compound of a metal with a weaker halogen displaces the latter; as when silver bromide is heated in chlorine, the bromine is displaced and may be allowed to escape and its weight calculated from the decrease in weight of the residue through the conversion of silver bromide (molecular weight 187.87) to silver chloride (molecular weight 143.37); or the bromine may be received in an absorbent and determined as usual. The operation is conducted in a combustion tube, the bromide contained in a porcelain boat.

After the evaporation of a solution to dryness, as a rule the residue may be redissolved by the same menstruum as formerly held it, but some compounds are so altered or decomposed during this operation, or the residue by its exposure to the temperature of 100°, as to remain insoluble, and the other soluble constituents be separable from it by lixiviation. Familiar examples of this transformation are silicic and tungstic acids. Where practicable, the above separation is usually the first step in an analysis of a complex mixture.

One of a mixture of several bodies may be decomposed at a temperature

* Chem. News, 1890—1—114.

† *Idem*, 1892—1—28; Journ. Amer. Chem. Socy. 1898—797.

above 100° becoming soluble or insoluble as the case may be. Thus if a solution of the chromates of cerium and lanthanum be evaporated and the residue heated to 110°, the cerium chromate is decomposed into insoluble cerium oxide and soluble chromic acid, while the lanthanum chromate is unaffected and may be lixiviated from the cerium oxide by water; on moderately heating a powdered mixture of lanthanum nitrate and didymium nitrate, only the latter is converted into the insoluble subnitrate; etc.

One of the constituents of a mixture may combine with a given reagent only at a temperature much higher than will the other constituents; or on raising the temperature of a solution, one of the dissolved salts may decompose and precipitate at a point much lower than the others. Thus, a solution of copper and silver nitrates mixed with magnesium carbonate and heated to 105° – 122° Fahr., the copper precipitates at once, the silver only after standing for some time.

Distillation. The separation of a liquid from a non-volatile substance, dissolved or diffused, is accomplished by simple evaporation, or by distillation if the liquid is to be preserved. A mixture of two immiscible liquids may be distilled and separated in the distillate by decantation, offering, for example, a means of resolving an emulsion obstinately resisting simpler methods of separation. And with a homogeneous mixture of volatile liquids a more or less complete separation may be had by distilling — a familiar example is the parting of ethyl alcohol (boiling at 78.4°) from water in the analysis of wine and spirits. It is of course essential that the boiling points of the members differ to a considerable degree in order to separate them in this way — the distillate of alcohol in the above example is always accompanied by water, though the proportion may be lessened, up to a certain point, by redistillation.

The coefficient of solubility of a gas in a liquid varies inversely with the temperature of the latter, and if the solution be raised to the boiling point and kept in ebullition for a time, the gas will be expelled more or less completely and may be collected in a gasometer or absorbed by a solution of some reagent.

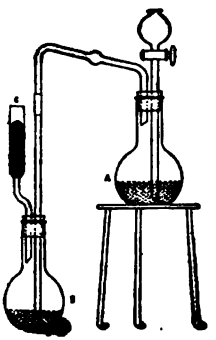

Fig. 73.

An apparatus for the purpose is shown in Fig. 73. The solution of the gas is placed in the flask A which is connected to the flask B containing a solution of the absorbent. A guard-tube C is filled with broken glass saturated with the absorbing solution. To assist in the evolution of the gas, a current of air or another gas whose admixture with the original is not objectionable, is drawn through the liquid in A entering at the funnel tube. Or a gas may be generated within the solution by the introduction of some reagent. Thus, a metallic sulfide in A may be decomposed by hydrochloric acid and the liberated hydrogen sulfide bubbled through a solution of silver nitrate in B, precipitating argentic sulfide to be further dealt with. If when the reaction is over, a solution of sodium bicarbonate is poured into A it will be dissolved by the excess of acid and generate a large volume of carbon dioxide gas, which passing out through B, carries with it the hydrogen sulfide that remains dissolved in the solution in A or fills the space in the flask above the liquid.

A method that is occasionally of service is that of distilling a complex mixture with some reagent that will mechanically or by chemical action, retain one or more volatile constituents in the still; thus in distilling a mineral oil with sodium bicarbonate, the sulfur is fixed by the alkali.

Fractional distillation (page 65) serves to approximately separate a number of allied volatile organic bodies from each other. A modification applied to organic acids is known as 'fractional saturation,' in which one or more of the members is united with a base to form a non-volatile compound from which the other acids are distilled. The acid with the greatest percentage of carbon in the molecule and the highest melting point unites with the base in preference to an acid of lower carbon and melting point; an exception is acetic acid. The process depends on the relative affinity for the acids to the base, both in the cold and at the temperature of distillation.

For example, both butyric and valeric acids readily pass over when their solution is distilled, while their alkali salts are not volatile at moderate temperatures. For separating them, to the aqueous solution of the mixed acids is added so much sodium hydrate as will surely be sufficient to combine with all the butyric acid, yet leave part of the valeric acid unneutralized. On distillation pure valeric acid passes over into the receiver. The residue of sodium butyrate and valerate in the still is treated with a little sulfuric acid to liberate more of the valeric acid, and the liquid again distilled. The acidification and distillation are repeated until butyric acid begins to come over, showing that all the valeric acid is in the receiver.

A similar plan may be adopted with a mixture of propionic, butyric, caproic, and caprylic acids. Practically, however, the separation is never as sharp as could be desired.

4. Precipitation. Where a choice of methods is allowed, that of precipitation is generally given the preference, for the reasons that the separation is, as a rule, complete enough for practical purposes, the manipulations simple, and the separated compound usually left in a form suitable for weighing.

The solvency of a liquid may be so far reduced that one constituent in solution separates unaltered. Alcohol precipitates dextrin from an aqueous solution; potassium chloride in concentrated solution is precipitated by hydrochloric acid; paraffin in mineral oil is thrown down by the addition of twenty volumes of glacial acetic acid; skatole is separated from indole when the mixture is dissolved in the least quantity of absolute alcohol and diluted with water; etc.

Many organic bodies are precipitated from an aqueous solution on the addition of a considerable amount of some inorganic salt ('salting out'), more completely if the solution be fully saturated by stirring with an excess of the powdered salt. Should the precipitate be a salt of a metal precipitable by hydrogen sulfide in a neutral solution, the filtered and washed precipitate may be suspended in water and the metal precipitated as sulfide; after filtering, the excess of hydrogen sulfide is removed from the regenerated organic body by boiling, fixation by an insoluble metallic compound, or transmitting a current of air or a gas.

On saturating a solution of several analogous bodies with a salt, some will precipitate only at specific elevated temperatures, and by slowly heating the solution and filtering at the proper temperatures, a fair separation is possible.

Two bodies may react with a third but one much more slowly than the other, so that by limiting the time of contact previous to filtration, one may be practically unaffected, the other completely transformed, and the two be separable by filtration or otherwise. Similarly the reaction with one body may be greatly hastened or retarded by raising or lowering the temperature or by other means.

When a mixture of liquids of different congealing points is cooled, the liquid of the highest melting point first solidifies and can be collected by expression through a cloth. This mode of separation is applied to the fats to remove stearin, to mineral oils for paraffin, etc., but the results are only approximate at best.

Crystallization. Many salts crystallize out more or less completely when their solutions are cooled, but the ratios of decrease of solubility to decrease of temperature are seldom so divergent as to allow of more than an approximate separation.

In fractional crystallization, the solution of several analogous salts is concentrated by evaporation and allowed to cool, whereupon the salt least soluble crystallizes, and as the mother-liquor is further evaporated another separates, and so on. Thus, the barium salts of the homologues of acetic acid crystallize in the order of the caprate, pelargonate, caprylate, oenanthylate, and caproate. This process, however, is but a beginning, as each crop of crystals is far from being unmixed with the others and must again be put through the same routine and its products also, so that the great number of repetitions demanded is wearying and the method resorted to only where no substitute can be found. The process is used in the separation of some of the rare earths, and for distinguishing the dextro- and laevo-rotary varieties of certain optically-neutral salts.

A precipitant may react with but one element or compound of a mixture to form a precipitate, or at the same time others be brought to an insoluble state but redissolved by the excess of the reagent. The separation in the latter case is seldom as complete as in the former since the permanent precipitate tends to prevent entire resolution, usually by inclosure or occlusion, though in some cases, undoubtedly, a true chemical union is established. As might be presumed, a considerable excess of the precipitant favors the resolution of the soluble part of the precipitate, sometimes to a remarkable extent, e. g., the separation of a ferric salt from salts of copper, chromium, etc., by precipitation with ammonia is only successful with a large excess of the alkali.

The completeness of a separation depends mainly upon the degree of insolubility of the precipitate and the solubility of the other constituents in presence of the excess of the precipitant; yet the tendency of the precipitate to occlude soluble matters, and their co-precipitation should be guarded against. With many elements a precipitation only may take place under widely varying conditions of concentration, temperature, acidity, etc., without affecting either the composition of the precipitate or lessening its insolubility. In a separation, however, these matters must be regulated more closely lest the precipitate retain a portion of the other constituents or itself partly remain in solution. When the bulk of the precipitate is relatively small and its aggregation granular, one precipitation may be sufficient, but when considerable in volume and gelatinous or flocculent, it is safer to dissolve it after filtration, and reprecipitate — provided that it is so insoluble that no considerable loss will be incurred.

Occasionally an insoluble precipitant is used for separations where it is necessary or desirable that no bodies be introduced into the solution other than are already present, or for other reasons. An example is the withdrawal of phosphoric acid in solution in strong nitric acid by metastannic acid formed in the solution by introducing metallic tin which is immediately oxidized by the nitric acid. Another is the indirect determination of a mixture of free formic and acetic acids by boiling the aqueous solution with mercuric oxide. The acetic acid dissolves an equivalent of the oxide, mercuric acetate passing into solution, while the formic acid breaks up to carbonic acid and water reducing an equivalent of the oxide to metallic mercury. The residue is treated with dilute hydrochloric acid which dissolves the excess of mercuric oxide and leaves metallic mercury ready for weighing.

Fractional precipitation presupposes a solution of two or more analogous

elements or compounds $a, b, c, \ldots\ldots$ each precipitable by a reagent r. Of the reagent there is introduced somewhat more than it is judged will saturate a, forming a precipitate of indefinite amounts of $ar, br, cr, \ldots\ldots$; but on standing for a time a replacement occurs, and the precipitate finally contains all of a as ar with more or less of br. After filtering, the remainder of $b, c, \ldots\ldots$ are precipitated in the same way. Obviously the separation is never exact even though each fraction be repeatedly redissolved and fractionally precipitated.*

For example, if a solution of the nitrates of lanthanum, samarium and didymium be fractionally precipitated by ammonia the first precipitate will be rich in samarium but also contain much didymium; the second precipitate is mainly didymium mixed with some lanthanum; and the third almost wholly lanthanum. Again, in the analysis of meat extracts, the gelatin precipitates when alcohol is added to the aqueous solution to the extent of 40 per cent by volume, albumose at 80 per cent, and peptones at 94 per cent.

Electrolysis is employed to dissociate a metal from an acid rest, and as a means of separation from metals not deposited by a current of moderate strength and from non-electrolytes. It is a neat and accurate method where available. Two metals can be separated at one time where one deposits on the cathode in the metallic state, the other on the anode as an oxide; or successively when their electrolytes are decomposable only under widely differing conditions (page (286).

5. Dialysis. This principle has some applications in organic analysis and toxicology. It utilizes the power possessed by the bodies known as 'crystalloids' of penetrating through a porous septum (e. g., an animal membrane), while other bodies known as 'colloids' do not pass through. To the former class belong the crystalline salts, and to the latter the proteids, gums, starches, gelatin, etc. The process can be used for the separation of inorganic colloidal compounds, such as silicic, molybdic, and tungstic acids, from crystalline salts, and to separate alkaloids from organic impurities or animal extractives. The same principle is occasionally applied to the separation of gases.

In one form of dialyzer a small glass hoop has a sheet of parchment stretched over the bottom forming a water-tight dish in which is contained the liquid to be dialyzed. It is half-immersed in a vessel of water, and after the lapse of some time, often several days, and with frequent changes of the water, the crystalloid will have passed out into the water leaving the colloid, although the separation is never quite complete. Other septa for the purpose are bisque-clay jars, and parchment paper made into tubes or thimbles.

A simple modification is due to Bauer.† A funnel is cut off a short distance above the stem, and a parchment filter fitted so as to project below the glass. The funnel is filled with the solution to be dialyzed and supported in a beaker of water. After severa changes of water the greater part of the crystalloids will have transpired.

As the rapidity of the diffusion is greater in proportion to the difference in concentration of the two liquids, time is saved by an arrangement to continuously remove the diffusate and supply fresh water. The stem of a funnel is closed by a rubber tube and screw pinch-cock; the solution to be dialyzed is held in a plaited filter of parchment paper, and the water conducted to the space between the paper and funnel by a rubber tube. The pinch-cock is opened so far that the water flows out in drops, and the water in the funnel is kept at the proper level by some automatic contrivance such as a Mariotte's bottle.

In general, a separation is most successful when the constituents bear to each other a comparatively small ratio by weight. When one of a mixture largely predominates and is precipitated or left insoluble, the others will often be occluded or mechanically held in part; and precipitation of a relatively small amount of one body in presence of a large amount of another is slower and may be less complete than if alone.

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* Speyers, Text book of Physical Chem 118.

† Chem. News, 1890—1—193.

The majority of analyses made for practical ends—of ores, commercial metals, pigments, oils, dyes, crude chemicals, etc.—call for the separation of the minor constituents or impurities from the greatly preponderating principal. Should a specific solvent or precipitant for each of the former be available, the separation presents no great difficulties; otherwise, a partial separation can often be made with advantage, dividing the original mixture into (1), the greater part of the major constituent in a pure state, and (2), all of the minor constituents mixed with the remainder of the major. Further separation of (2) is proceeded with by suitable methods, facilitated by the presence of only a relatively small proportion of the major constituent. Such a preliminary separation may be done in various ways.

1. A partial solution of the major constituent may be effected by a suitable solvent, provided always that the minor constituents or impurities are practically insoluble both in the solvent and its solution of the principal constituent. If not highly insoluble and a correction for solubility is attempted, that the solution of the principal constituent is quite concentrated in regard to the latter, must not be forgotten. The principal constituent must dissolve freely in the solvent, as if only moderately soluble the separation is less exact.

When the greater part of a commercial metal is dissolved by an acid the more electro-positive impurities remain insoluble, as when bar-lead is nearly dissolved in dilute nitric acid, the silver it contains is concentrated in what remains.

Or a solvent may be chosen in which the main constituent remains almost entirely undissolved. For powdered commercial metals, alloys and amalgams, the solvent may be a solution or suspension of a salt of the major constituent, the base of the salt replacing the minor constituents which pass into solution. The method is more successful where the latter are in separate grains or crystals mixed with those of the former and the substance finely powdered than with alloys.

2. Partial crystallization. Where the minor constituents are much less soluble than the major, perhaps the most successful plan is to prepare a concentrated solution, evaporate until crystals begin to form, and filter while the solution is hot. As soon as a small amount of crystals form in the filtrate through its slow cooling, it is again filtered, and this process is continued until from the color, shape, or other appearance of the crystals or by qualitative tests, it is seen that the mother liquor is free from the minor constituents. The different crops of crystals are united and the further separation proceeded with by a different method.

Sometimes the members of a mixture of crystallizable acids or bases may not differ in solubility so greatly as to make possible a partial separation by the above method, but by combination to salts with a suitable base or acid radical, the requisite difference will be obtained.

Should the major constituent be less soluble than the minor ones, as much as possible of the former is crystallized out, the crystals redissolved and the operation repeated once or oftener. The mother liquors are united and further treated. Possibly a process analogous to that of fractional distillation (page 65) may repay the time and labor required.

3. Partial precipitation. A precipitant that has a common but selective action for the various constituents is added to their solution in quantity only sufficient to throw down either the greater part of the major constituent alone, or all the minor constituents mixed with some of the major, the amount greater or less as the composition of the original mixture was known and the proportion of the precipitant limited accordingly. For example, from a solution of a manganous salt containing a little ferric salt, ammonium sulfide precipitates first the iron, later the manganese. The contrast in color between the iron and manganese sulfides is so marked as to indicate when all the iron has been pre-

cipitated. However, this method is not to be depended on where the minor constituents of the mixture bear less than a certain proportion to the major.

Another method is to react with the minor constituent by introducing into the solution some sparingly soluble compound of the major constituent. Thus, to a solution of much potassium chloride and a little rubidium chloride is added the slightly soluble compound potassium platinchloride; this reacts only with the rubidium, precipitating rubidium platinchloride, an equivalent of potassium passing into solution.

4. Other principles may be employed as the nature of the mixture indicates.

DECANTATION — FILTRATION — WASHING.

The separation of a precipitate from the liquid in which it has been formed is an operation common to most analyses; and frequently the collection of a residue left after partial solution of a solid, or the parting of two immiscible liquids is called for.

Obviously the most direct procedure is to allow the solid to collect and pour off the supernatant liquid, but in practice this simple and convenient means is restricted to residues and precipitates of the heavier metals or acid radicals, or those formed in light liquids, and to some organic bodies that form a viscid mass or adhere closely to the interior of the vessel.

In dealing with a metal precipitated as a spongy mass or left as a powder after extraction of another metal alloyed with it, the liquid is cautiously decanted, and the remaining small amount displaced by agitating with water and pouring off until the metal has been washed practically clean. Both the decantations and washings are examined after standing for a time that any particles of metal carried over may be detected and recovered. The metal is washed into a light tared dished or flask, as much of the water decanted as possible, then rinsed once or twice with strong alcohol, dried at a gentle heat, and weighed. The final drying is done in a current of some reducing gas should the metal be readily oxidizable by the air.

Since the residue or precipitate should be disturbed as little as possible during the decantations and washings, the operation is best performed in a tall glass vessel shaped like the 'precipitating jar', Fig. 74, the body merging abruptly into the bottom. The powder collects in the angle as the jar is inclined, allowing nearly all of the liquid to be poured off, and the conical shape also tends to the collection of the precipitate at the bottom. Where the volume of the supernatant liquid is greater than can be conveniently decanted it is drawn off by a narrow glass syphon or a large pipette.

Fig. 74.

Precipitates, residues from partial solution, and suspended matter in general, if small in bulk and held in a moderate volume of liquid, can be made to deposit quickly and in a compact and coherent mass by the aid of centrifugal force.

The turbid liquid is transferred to a thick-walled test-tube, best having the bottom drawn into a conical shape; small flasks or beakers of heavy glass may also be used in special machines.

The centrifugal machine, 'centrifuge' or 'whirl' is essentially a vertical iron shaft provided with a mechanism at the bottom by which it can be rotated at a high speed. The power may be a geared hand-crank or a small electric or water motor. From the upper end of the shaft project a number of horizontal radial arms symmetrically disposed; to the outer end of each arm is hinged a holder, a metal cup of such a size and shape that the test-tube fits

snugly within. Being hinged, the holders hang vertically when the machine is at rest, but when the shaft attains a certain speed they rise to a horizontal position, the mouth of the test-tube inward.

Through the centrifugal force imparted by the rapid circular motion, the liquid is held in the test-tube, and a precipitate of a specific gravity greater than the liquid is thrown to the bottom of the test-tube where it eventually coheres to a more or less compact layer leaving the liquid perfectly clear. Frequently the cohesion of the particles is so marked that the liquid can be entirely decanted without rousing the precipitate.

The time required for the deposition and the compactness of the deposit depends on the speed of the machine. From five to ten minutes rotation at from 1,000 to 5,000 revolutions per minute will usually be sufficient for the purpose.

Purdy's machine, Fig. 75, is specially designed for the analysis of urine. Within the base is a small motor wound for an ordinary incandescent light current and is connected to a socket by flexible conducting wires. The two sheet-metal holders at the extremities of the cross-bar are hung to it by pivots and have the shape of the test-tube contained.

Gaertner's centrifuge has a central shaft supported on pointed bearings at the extremities. Fixed near the bottom is a disk sloping outward at an angle of about 30° from the horizontal. On the disk are a number of spring clamps for holding the test-tubes, and a cover screws down over it. A long cord is wound around the shaft and the free end forcibly pulled away. As the cord unwinds, the shaft is impelled to rotate for several minutes at an initial high speed.

Fig. 75.

The centrifuge is found very useful in technical work, and many of the quick and fairly accurate tests of urine, milk, sugar, etc., are due to its aid.

The thin coating of a metal deposited by electrolysis on a smooth platinum sheet is so compact and firmly adherent that decantation of the solution and washing can be done with the greatest facility, but with some metals and solutions it is required that the solution be poured off and the deposit washed while the electric current continues to pass between the electrodes, as if interrupted, the surface of the deposit would be redissolved. For this purpose, a syphon made of a narrow glass tube is filled with water and the lower limb closed with the finger, then the shorter limb is lowered into the solution. As the liquid is drawn up from the bottom of the vessel, water is gently poured in against the side, the greater density of the solution preventing their mixing to any great extent.

Some organic bodies are thrown out of solution in the form of clots that on stirring the solution become so tenaciously attached to the sides of the vessel that the liquid may be poured off perfectly clear. In this case the vessel is commonly a light tared Erlenmyer flask, and after decanting the solution and washing the precipitate, the latter is dried by blowing in a current of dry air, the flask heated gently meanwhile provided this is not contraindicated. The increase in weight of the flask gives the weight of the precipitate.

It often happens in technical analysis that some element or body whose determination is not required, is to be separated by precipitation. To save the time of filtration and washing or for other reasons, the clear cold solution may be poured into a measuring flask followed by the precipitant. After mixing well, the turbid liquid is made up to the mark with water, again well shaken, and allowed to settle. The greater part of the clear supernatant liquid is

poured off, and measured portions, aliquot parts of the volume held by the measuring flask, are used for the necessary determinations as though each was the entire filtrate. The liquid may be conveniently drawn out by a small burette from which several fractional parts may be tapped for separate examination.

The space occupied by a precipitate or residue of apparent moderate bulk is often so small as to be neglected with safety, for many seemingly voluminous precipitates are so attenuated that they in reality displace but little of the liquid. If the bulk is considerable in relation to the volume of the supernatant solution, a correction must be found and applied; it may be roughly determined by mixing measured volumes of the clear solution and precipitant in a tall measuring jar and noting to what extent their united volume is exaggerated by the precipitate produced.

A more accurate plan is as follows, on the principle that the more dilute the supernatant fluid, the less is any property thereof altered by the space occupied by a precipitate; in other words, the concentration of the supernatant fluid varies in a direct ratio with the volume of the precipitate, the ratio of increase being less, the more dilute the fluid. One method is to make up the turbid liquid to a certain volume V and after settling to draw off an aliquot part V' and determine therein the value of some constant a. The remainder of the liquid in the flask is again diluted to V, the volume V' withdrawn, and the same constant again determined giving b. Then if m is the concentration of the original solution, and x the volume of the precipitate, $\frac{m\,V'}{V-x} = a$; and $a : m :: b : m - a$. Whence $x = V - \frac{a\,V'}{a-b}$.

The datum to be secured may be either a physical constant or the proportion of some one or more constituents — the weight of the residue left on evaporation of the solution is often convenient. It must be known, however, that the value of the physical constant determined is not altered beyond the normal by dilution.

For technical work on special commercial liquids, vegetable extracts, saps, etc., flasks may be purchased that are calibrated to hold a standard volume of the liquid plus the volume of a certain precipitate formed therein or an insoluble residue, obviating the necessity of a correction for the latter.

With precipitates that are slow to settle, instead of decantation, the bulk of the liquid can be filtered through a dry paper. Exceptions are highly volatile liquids, where the unavoidable evaporation would increase their concentration. But precipitates settle more readily and can be decanted from more easily when formed in a light volatile liquid than in an aqueous solution.

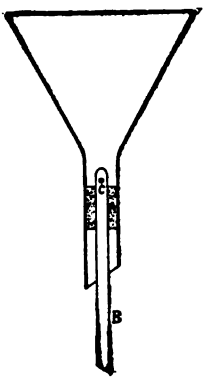

Fig. 76.

To part two immiscible liquids, as an oil from a watery solution, the mixture is poured into a separatory funnel, Fig. 70. The stem should be short and wide, and cut off obliquely that it may readily empty, and the funnel have a narrow bore for a short distance above the stopcock. The lower stratum is drawn by the tap from the upper layer, and if necessary, the latter washed by alternately agitating with water or some solution and drawing off when the layers have formed. The traces of oil always carried off in an aqueous solution are recovered by shaking the latter with an organic solvent, then separating as above.

Fig. 77.

A simpler form of separator without a stop-cock is shown in Fig. 76. In the wide stem

of a funnel is a tighly fitting cork A, through it passing a glass tube B. The top of the tube has been sealed, and perforated at C with a small hole by heating the tube at that point with a fine blowpipe flame and applying suction at the open end. The tube is inserted in the cork only so far that C is below the top of the cork. The mixture of liquids is poured into the funnel, and when stratification has taken place the tube is pushed up until the hole just appears above the cork, retracting the tube as soon as the lower layer has run out through B.

In another contrivance the liquids are held in a test-tube closed by a loosely fitting cork through which passes a pipette, Fig. 77. After the liquids have separated, the pipette is adjusted until the lower orifice nearly reaches the surface of the lower layer; the upper layer is then withdrawn by suction. A long-rubber tube passed over the top of the pipette will facilitate the operation.

FILTRATION.

But it is the exception that a precipitate or residue is so dense, heavy and coherent that the liquid may be decanted or syphoned perfectly clear, so that a medium must be interposed whose pores are so minute as to retain solids, even in fine powder, yet not obstruct the rapid passage of a liquid.

The nature of both the solid and the liquid must be considered in the selection of a filtering medium. The precipitate may be curdy, like silver chloride; gelatinous, like aluminum hydrate; crystalline, as ammonium manganous phosphate; or pulverulent, as barium sulfate; frequently shrinking or crystallizing on standing from a voluminous flocculent condition to a dense pulverulent form; while a residue left after the partial solution of a substance may resemble any of the above, or if complex in character, a mixture of two or more. The supernatant liquid may be acid, neutral or alkaline, dilute or concentrated, hot or cold. To meet these widely different conditions, various media for filtration are in use.

Paper. We have in unglazed paper a material well suited to the majority of filtrations. For quantitative analysis it is prepared from linen or a mixture of linen and cotton, undergoing an elaborate treatment during its manufacture to eliminate foreign matter and give a product of almost pure cellulose. An analysis of a German paper showed: —

Moisture at 100°	5.36
Ash	.87
Hydrocellulose, soluble in alcohol	.73
Lignin, etc	None
Cellulose	93.69

Much of the inorganic matter or ash (chiefly silicates of calcium and iron) may be dissolved out of the paper, or the pulp during the manufacture, by hydrochloric acid, and practically all the remainder by hydrofluoric acid. Through the previous elimination of the ash, its introduction into an acid fluid during filtration is avoided, and when a filter is burned with a precipitate, this "extracted" paper leaves so small a proportion of ash that no account need be taken of its weight even from the larger sizes of filters.

All grades of paper can be purchased in large sheets of different thickness and closeness of fiber, or ready cut in circles of various sizes, either extracted or untreated. The best known manufacturers are J. H. Munktell, of Gryksbro, Sweden; Carl Schleicher & Schuell, of Duren, Rhenish Prussia; and Max Dreverhoff, of Dresden; their products are also acid extracted by several European and American firms who market the washed paper under their own trade-marks.

Other conditions being the same, the rapidity of a filtration is governed more by the compactness of the fiber than the thickness of the paper, a thinner

variety being often less readily permeable than a heavier one. For quantitative analysis it is well to keep in stock several grades of paper — one for general work, one for finely divided precipitates, and one for precipitates that have a tendency to clog the paper. For general work may be recommended the S. & S. Nos. 595, 597 and 598, the Munktell Nos. 2 and 3, and the Dreverhoff No. 480; and the extracted paper S. & S. Nos. 589 and 590, Munktell Nos. 0 and 00, and Dreverhoff Nos. 400 and 418. To retain the finest precipitates S. & S. No. 575, 602, and 589 "blue ribbon" or Munktell No. 100, and for oils, juices, etc., S. & S. No. 584 or 591, or Dreverhoff No. 260. The sizes mostly used in analysis are 9, 11 and 12.5 cm. in diameter.*

Or the chemist may purchase the paper in sheets and extract it with acid. The bottom of a bottle is cut off and a rubber tube with a pinch-cock joined to a glass tube passed through a cork in the neck. The paper is cut into circles of the proper sizes and digested over night with dilute hydrochloric acid; then washed with distilled water, thoroughly, since if a trace of acid remains, the dried paper will be found brittle and worthless.

Many specially prepared papers are now manufactured, or have been suggested, designed to meet the requirements of the technical chemist. Starch-free and fat-free papers are on the market for use in the analysis of materials containing these bodies, in the form of circles, strips for coiling, and thimble-shapes for extraction. It has been proposed to utilize the decolorizing property of animal charcoal, and the absorptive power of hide-powder for tannin and the like, by mixing a certain proportion of these in the paper-pulp. The paper may be hardened or toughened sufficiently to resist the pressure of the filter pump by treatment with nitric acid, or the pulp partially or entirely converted into nitro-cellulose which is said to filter more rapidly as well as burn more quickly than the untreated.

To support the paper during filtration, funnels made of chemical glassware are almost invariably employed. The interior should be a true cone at an angle of 60° or nearly so, and the stem narrow and uniform in bore that it may fill with the liquid during filtration. They are held in a wooden stand, Fig. 78, of which the best form has the supporting arm of sufficient breadth to cover the beaker receiving the filtrate, protecting it from dust; if too narrow for this purpose the beaker, as well as the funnel, is covered by a watch-glass.

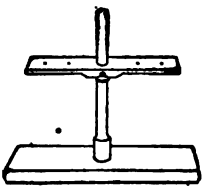

Fig. 78. 1/18

It is sometimes necessary to keep the contents of the funnel hot during a filtration — as when a melted fat is to be clarified to avoid the danger of the less fusible stearin solidifying and remaining on the filter while the liquid olein passes through, or to prevent a solution of a soap from setting to a jelly. Here the funnel is encased in a double sheet-metal jacket containing water or a salt solution kept boiling by a burner beneath a projecting arm.† If, on the other hand, the contents must be maintained at a lower temperature than that of the laboratory, as in dealing with a precipitate whose solubility decreases with the temperature, the funnel is surrounded by a coil of metal pipe through which circulates ice-water or chilled brine.

Porcelain, hard-rubber, and stone ware funnels have an occasional use in special technical analyses.

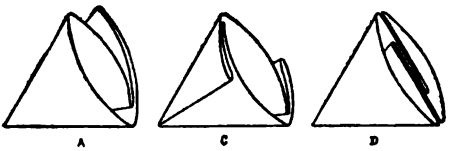

Fig. 79.

Filtration. A paper is chosen so large that the precipitate will not more than half fill it and the circle folded into a quadrant as at A, Fig. 79. A

* "These filters must satisfy the highest pretensions of the most painful analytical chemist."

† Chem. News, 1894—1—60.

glass funnel is selected whose slant height is at least one-quarter of an inch greater than the radius of the filter; if it be of an angle of exactly 60° the filter will fit snugly throughout, but as few funnels can be found that are not of a greater or less angle, the paper must be folded accordingly. After moistening with water, any air-bubbles beneath the paper are pressed out by the fingers. The funnel is inverted and the stem filled with water from the wash-bottle.

Other ways of folding are shown at C, and D which allow a more rapid filtration — the re-entrant folds of D are held to place by a bent glass rod.* It is well for future use to make two file marks on the edge of each funnel showing how far one fold of the paper should overlap at the edge to insure a perfect fitting filter.

Much time will be saved by allowing the precipitate or insoluble matter to settle before filtration, and retaining it in the beaker as far as can be done until the liquid has passed through the filter. To prevent splashing, a glass rod with rounded ends will assist in directing the stream against the paper near its edge; and the orifice of the stem of the funnel should touch the side of the receiving vessel. When as much as possible of the liquid has been run through, the precipitate may be washed by decantation or brought directly on the filter, flushing out the last portion by holding the beaker in an inclined position over the funnel and directing a stream of water from the wash bottle around the interior.

Usually the precipitate is heavier than the liquid surrounding it and sinks to the bottom; in the few instances where the liquid is the denser, the precipitate may be caused to sink by dilution with water.

Strainers of muslin or linen cloth or chamois skin and conical bags of felt are of occasional use for removing gross particles from a vegetable extract or similar liquid, and a small filter-press may serve to hasten the operation. From the large amount of material used in examinations of this kind, small mechanical losses are not of so much consequence.

A plug of cotton-wool, best of the kind sold for surgical purposes as "absorbent cotton" is used to close a funnel stem or percolator. It is only suitable for straining out coarse particles, as if compacted enough to retain fine powders the filtration becomes very slow on account of the small surface exposed.†

Fig. 80.

Other filtering mediums. Concentrated mineral acids, strong alkali solutions, and powerful oxidizers like chromic acid and the permanganates destroy or are acted on by paper and other organic filters, and for these liquids there is chosen some inorganic substance that is unaffected. A medium free from carbon is used for organic residues and precipitates that are to be afterward subjected to an ultimate analysis without removing from the filter.

The mineral asbestos (actinolite) is practically unaltered by contact with chemical solutions including the acids (hydrofluoric excepted), though long digestion with strong acids will dissolve small amounts of the constituents of the pure mineral. It is infusible up to a white heat. Unlike those of vegetable origin, the filaments cannot be felted into thin sheets, so that a filter is prepared by cutting the asbestos across the fiber into short lengths and boiling with strong hydrochloric acid to extract any oxide of iron, soluble silicates, etc., that may accompany the mineral. The disintegrated fibers are then stirred up with water.

* Chem. News, 1889—2—102.

† Crookes' Select Methods, 671.

In a funnel or carbon tube is laid a disk of platinum gauze or a circular plate of glass or porcelain perforated with numerous fine holes, of such a diameter as to rest a short distance above the funnel stem. As the disk is apt to be displaced during filtration, it is safer to substitute for it a flat closely rolled coil of heavy platinum wire, Fig. 80, the inner end bent at a right angle to the coil and extending through the funnel stem, thus preventing the coil from being more than slightly tilted.

The asbestos pulp is poured in the funnel until, when the water has drained away, there is left a layer of fibers one-eighth inch or more in thickness. Water holding in suspension the finest particles is then poured in until the layer is covered by a thin close film that will retain a finely divided precipitate. During the filtration the liquid and wash-water must be run into the funnel carefully in order that the asbestos may not be disturbed. Usually the funnel is a part of the vacuum filtering apparatus (page 93), and in this case the precaution is of less import, as the asbestos is held to a more compact condition by the pressure of the air.

The Gooch crucible, Fig. 81, is made of platinum, sometimes of porcelain, and has a flat bottom perforated with many fine holes. During a filtration the crucible is held in a funnel by the aid of a wide rubber band drawn over the edge. The funnel stem is inserted in the cork of a filtering-flask or bell-jar connected with a vacuum-pump, and the bottom of the crucible covered with a layer of asbestos as described above, of a thickness of from one to five millimeters according to the texture of the asbestos and the fineness of the precipitate to be held. After preparing the crucible it is ignited and weighed before filtration.

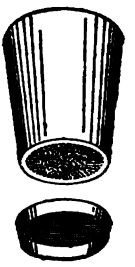

Fig. 81.

For filtering an organic residue or precipitate that is to be submitted to an elementary analysis, a platinum boat with perforated bottom and held in a funnel of the same shape is prepared in the same way as a Gooch crucible. After filtration and washing the boat can be inserted bodily into a combustion tube without need of transferring the contents.

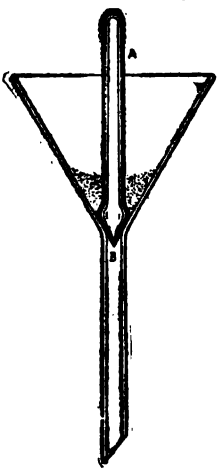

Fig. 82.

As substitutes for asbestos there have been proposed anthracene precipitated in floccose tufts, it being insoluble in most reagents except the strong acids and some organic liquids, and is entirely volatile at a moderate heat; and a metallic felt, such as spongy platinum, a layer formed in the crucible by packing in ammonium platinic chloride, then driving off the ammonium and chlorine by heating to redness.

Glass-wool (matted filaments of Bohemian glass) gives a filter so open in texture that it is adapted only to the straining of precipitates of the coarsest nature. For certain purposes a layer over or under an asbestos felt affords a quick filtration and a clear filtrate. A thin jar of unglazed clay or porcelain retains the most finely divided matter (even bacteria are held) but is mostly used for clarification only, or where corrosive liquids are to be filtered.

Sand or powdered glass or quartz is the medium in a few filtrations where the precipitate is fairly coarse and is to be redissolved after filtration and washing. A glass rod A, Fig. 82, greater in diameter than the bore of the stem of the funnel has its lower end drawn out into a conical point B which closes the apex so nearly that while a fluid readily passes, the particles of sand heaped around it are retained. After filtration and washing, the rod is withdrawn and the precipitate and sand flushed with water through the stem into a beaker. For volumetric analysis the admixture of sand with the precipitate is of no consequence.

Rapid filtration. Even under conditions the most favorable, a filtration takes considerable time and attention and is especially tedious when dealing with gelatinous and slimy precipitates, or with liquids slowly evolving gases. A number of devices have been proposed to hasten the passage of the liquid through the filter, such as applying centrifugal force in a centrifuge, increasing the pressure of the air on the liquid in the funnel, etc. But two of these are in common use. In the first, the funnel stem is lengthened to the extent of a foot or more by attaching a narrow glass tube with a loop near the middle; as the tube fills with the filtrate, the column exerts a tension proportionate to its length.

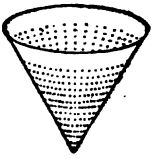

Fig. 83. 1 to $^1/_3$

The second is the well known invention of Bunsen, utilizing the pressure of the atmosphere on the surface of the liquid in the funnel by maintaining a more or less complete vacuum in the funnel stem. It has three essential parts; a funnel and cone for the filter, an air-tight receiver for the filtrate, and a pump to exhaust the air.

The funnel should be very nearly of an angle of 60° since the apex of the moist paper is too weak to withstand the increased pressure and must be supported by a perforated cone of that angle made of sheet platinum, Fig. 83, and the filter folded to fit both. Or the cone may be nearly as large as the interior of the body of the funnel, a flange from the edge resting on the edge of the funnel with a soft rubber gasket interposed to make the junction air-tight.

Another device is a flat circular plate of slightly less diameter than the funnel-rim and profusely perforated with small holes. The plate lays horizontally in the funnel a short distance below the rim, and on it is laid a circle of filter paper of slightly greater diameter. In an improvement the edge of the plate has a peripheral U-shaped groove in which is held a rubber ring to make an air-tight junction between the plate and funnel.

The funnel-stem passes through a cork or rubber stopper inserted in the neck of a flask of thick glass with a side tube connecting with the pump, or of a tubulated bell-jar resting on a ground-glass plate and inclosing a beaker, Fig. 84. The filtrate passes through the funnel stem in alternate bands of liquid and bubbles of air, and as the latter emerge from the orifice, tend to spatter the liquid in all directions; for this reason the stem should be of sufficient length to reach well into the beaker, passing through a small hole in a watch glass covering it. Or a small inverted funnel may be closely attached to the stem by rubber tubing.

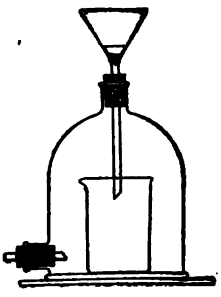

Fig. 84.

In the modification of the filter flask described by Walther,* the neck is expanded to a conical shape conforming to the usual angle of glass funnels. Between the expansion and the body of the funnel is placed a rubber ring. Advantages are that no cork is needed and funnels of different sized stems are accommodated equally well.

The pump for exhausting the air is made of glass or brass on the principle of the trompé or Sprengel's

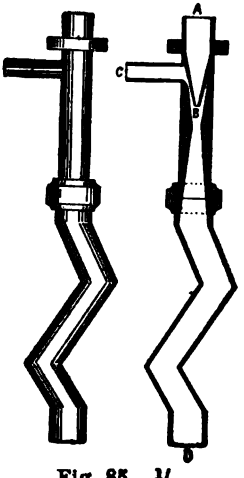

Fig. 85. $^1/_4$

* Analyst, 1898–305.

mercury pump. Fig. 85 shows in section an efficient and rapid working brass pump designed by Richards. The inlet is threaded for screwing to a faucet delivering water under pressure. The water enters at A and as it passes the contraction in the tube at B drags air from C with it, the foam flowing out through D. C is joined by rubber tubing to the filtering flask; an empty wash-bottle may be interposed between C and the filtering flask for the purpose of intercepting and retaining any water drawn back from the waste-pipe below D, which may happen when the water supply is suddenly checked.

Chapman's filter pump is somewhat slower in action than Richards', but gives eventually a remarkably complete exhaustion under favorable conditions. A rubber valve in the pump serves the purpose of the empty wash-bottle.

A blast of steam or highly compressed air will answer as a substitute for the stream of water.

The tension of the vacuum obtainable with a pump of the above description is governed mainly by the rapidity with which the water flows past B, this depending on the initial pressure and the vertical length of the waste-pipe. In practice, by reason of leakage of air through and around the filter and elsewhere, the tension in the filtering flask is seldom reduced below half an atmosphere; however, a higher exhaustion is not often required in ordinary analytical work.

Various devices may be adopted to obtain a moderate vacuum where a flow of water is not available, and for a description of these reference may be had to the original papers.

A filter paper is folded to exactly fit the funnel, inserted and moistened with water. The pump is then started with a stream so slow as to give only a moderate vacuum — a higher one is apt to tear the paper or clog it with the finer floating particles of the precipitate. When all the precipitate has been transferred to the filter and before it has shrunken, the washing fluid is poured on from a beaker. The vacuum may be then increased to the full capacity of the pump, when two or three additional washings will suffice, since the atmospheric pressure drives the wash-water through so rapidly that there is but little diffusion of the adhering part of one washing into the following one. The pressure compacts the precipitate to only a small fraction of the apparent original volume.

Advantages. As the great merit of this device lies in the rapidity with which precipitates may be filtered and the facility of their washing, it is especially acceptable in technical work where time is so important a consideration. Yet instances are not few where its employment is certainly unadvisable — the tendency of some slimy precipitates to compact to an almost impervious varnish against the filter increases with the pressure, as does that of finely divided ones to run through a paper of ordinary porosity; moreover the precipitate cannot so well be protected from dust and laboratory fumes by covering the funnel as in the ordinary method of filtration. On the whole the student will do well to adopt the older plan until he has become familiar with the behavior of precipitates of different aggregation and the best way of dealing with them.

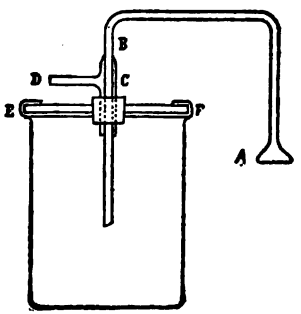

Fig. 86.

In Carmichael's device, Fig. 86,* for upward filtration, a long glass tube A B is twice bent at right angles. One limb passes at B through a T-tube C D. Terminating the other limb is a small rose or bulb A flattened beneath to a circle about an inch in diameter which is per-

* Crookes, Select Methods, 665.

forated by many fine holes. The receiving vessel is a beaker with edge ground flat, closed by a glass plate E F, and exhausted through a connection of the branch D of the T-tube with a vacuum-pump, air-tightness being secured by rubber tubing and sheeting.

A moistened filter paper of the same diameter as the bulb is pressed against it, the pump is started, and the bulb lowered into the dish containing the solution to be filtered. After filtration the precipitate is washed by pouring water into the dish.

The apparatus of the size described is only suited to small precipitates. It is recommended that the precipitation be done in a small tared platinum dish, and after washing, the paper and adhering precipitate blown back into the dish ready for drying or ignition and weighing.

Filtration of liquids and gases. Two immiscible liquids can be parted by filtration through paper or other medium. Before pouring in the mixture the filter is wetted by the same liquid as the heavier of the two, and throughout the filtration it should always contain some of the heavier liquid, as otherwise part of the lighter may also pass through.

The filtration of a fat or fatty acid from an aqueous solution may also be done by cooling the mixture to the point of solidification of the former, with constant stirring. The disintegrated particles are readily filtered through paper by a light suction, and on washing with cold water show no tendency to pass through.

Gases are freed from suspended soot or fume by passage through a scrubber, usually a long U-tube packed with moist cotton or asbestos.

A pulverulent precipitate, especially when but recently formed, may be so finely divided as to pass through the pores of even a thick or specially prepared paper. It may save a refiltration to replace the beaker receiving the filtrate by another, after decanting the clear liquid but before transferring the precipitate to the filter, and should the filtrate or washings be turbid, to return it to the filter until what it passes is perfectly clear.

When it is anticipated that a precipitate is so finely divided that it will pass the paper: (1), two filters should be used, inclosing one within the other with the plications counterposed so as to bring the single thickness of the interior against the triple fold of the exterior. Sometimes a triple filter of the ordinary quality is safer, although one paper of a specially close texture (such as the Dreverhoff's No. 400), or paper that has been indurated may answer; (2), after decanting the clear fluid, the precipitate may be stirred up with some inert fibrous or gelatinous substance to entangle the fine powder, such as cellulose (prepared by beating up filter paper with strong hydrochloric acid and washing the residue); recently precipitated aluminum hydrate; albumin, to be subsequently coagulated by boiling the solution; or a few drops of collodion, water precipitating the pyroxylin from its alcohol-ether solution; (3), heating the fluid before or after precipitation causes the finer particles to coalesce to larger ones; moreover a hot liquid always passes through paper more rapidly than when cold by reason of its lessened viscosity; (4), colloidal precipitates filter clear when a certain proportion of an inorganic salt is dissolved in the supernatant liquid. The character of the precipitate and the after treatment intended will determine which, if any, of the above may be adopted.

On the other hand, many precipitates and residues are of a nature tending to clog the pores of the paper and retard the filtration to an annoying extent. Ribbed or corrugated filters, funnels internally fluted, and other devices to interrupt contact of the paper with the glass, while materially hastening filtration, are, from the difficulty or impossibility of thoroughly washing the precipitate and filter, limited to such filtrations as require only the examination of an aliquot part of the filtrate.

Generally, such precipitates are best handled by heating the fluid before precipitation, afterwards boiling for a short time — long boiling is apt to cause the precipitate to become slimy. The washing is done by decantation keeping the precipitate in the beaker, as far as may be, until the washing is nearly completed. As in the case of a pulverulent precipitate, a vehicle may be intermixed with the liquid, but here a dense powder like silica, kaolin, magnesia or calcium carbonate, though it must always be predetermined that no soluble matter is absorbed by the powder from the solution.

When a liquid or precipitate must be shielded from the oxygen of the air during filtration, a device similar to the Carmichael filter (page 94) may be fitted to a wide-mouth bottle through the cork of which passes also a tube conveying a current of some non-oxidizing gas, and a funnel-tube to introduce the precipitant and wash water. In filtering dilute solutions of the caustic alkalies or the earths, a jet of hydrogen played over the surface of the liquid in the filter is a sufficient protection from the carbon dioxide of the air.

WASHING OF PRECIPITATES.

After filtration, the impurities from which a precipitate or residue must be freed before it is weighed may be: —

1. Mechanically adherent or entangled; as a solution of sodium phosphate to a precipitate of calcium phosphate, or inclosed in a curdy or gelatinous one, as sodium chloride in chromium hydrate.

2. Suspended matter or colloidal bodies carried down by the precipitate.

3. Co-precipitated by some secondary reaction; as in the separation of ferric chloride from manganous chloride by ammonia, where the ferric hydrate always contains some manganic hydrate formed by the decomposition of the soluble ammonium manganous chloride by absorption of oxygen from the air; sulfur accompanying a metallic sulfide; etc.

4. Chemically combined in the form of a double salt or other complex; as when lead acetate is compounded with potassium sulfate, there is precipitated potassium lead sulfate which is but slowly decomposed by water into the simple sulfates.

The impurities of (1) can usually be removed by sufficient washing with water or other fluid, though sometimes only completely after a structural change in the precipitate; those of (2) and (3) usually only by solution of the precipitate and reprecipitation; and of (4) by one or the other of these according to circumstances.

Washing. As a rule, the smaller the proportion of any body in solution, the less it tends to contaminate a precipitate formed therein, so that, other conditions being the same, a precipitate will be purer the greater the volume of the solution from which it falls; this in addition to the influence of high dilution toward the slow collection of a precipitate, a condition favorable to purity. But we are restrained from any considerable dilution of the liquid on account of the loss incurred through the greater or less solubility of all precipitates, not to speak of the time lost in concentrating the unwieldy filtrate previous to further treatment, and so are restricted to dilution of the fluid immediately surrounding the precipitate after the major part of the liquid has been decanted through a filter. By successive dilutions and decantations the soluble impurities are rapidly reduced to the point of practical, though never entire, elimination. Tables have been published showing the rate of this reduction when the bulk of the precipitate and volume of water used are approximately known, and the number of times a given precipitate must be washed with given volumes of water to practically free it from impurities; but owing to differences

in the structure and agglomeration of precipitates formed under varying conditions, and other factors, they are of little practical value.

Water is used for the detersion of a precipitate formed in an aqueous solution, unless debarred (1), by its solvent effect, when another fluid or a solution is substituted, as alcohol for calcium sulfate, ether for some alkaloids, or a saturated solution of the same compound as the (sparingly soluble) precipitate to remove impurities from an alkaloidal salt; (2), by allowing oxidation — many metallic sulfides must be shielded from the air by saturating the wash water with hydrogen sulfide; (3), by its action to hydrolize or decompose the precipitate, as barium stearate resolved by water into baryta and stearic acid; or (4), by its tendency to disintegrate colloidal precipitates which lose their original coherency and incline to run through the filter — with these must be used a dilute solution of some salt, preferably one of ammonium if the precipitate is to be afterward ignited and weighed.

Certain impurities, soluble but firmly adhering to the precipitate, may be transformed by a suitable reagent in the washing fluid to another soluble combination and pass entirely into the washings. The purification of the precipitate is to be credited rather to the effect of a physical change destroying the adhesion than to the superior solubility of the new compound. Even insoluble impurities, if in small amount, may be changed to soluble forms and washed out, though the chances of failure are greater than in the former case. Similarly, a washing fluid may be so compounded as to induce a physical change in some precipitates — as from flocculent to pulverulent, or amorphous to crystalline — and free occluded or adherent impurities.

An alternation of two different washing fluids is sometimes of advantage. One of the impurities to be washed out may be freely soluble in the first and but sparingly in the second, another the reverse; an impurity may be present that tends to decompose with the first to some insoluble form and must be brought back to its original soluble combination by the second; an undesirable physical change in the precipitate may be wrought by the first and the original condition restored by the second; etc.

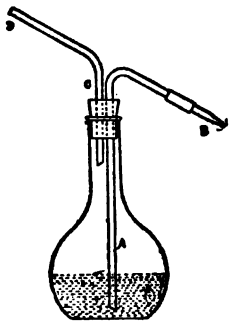

Fig. 87.

Wash-bottle. A stream of water is furnished by a wash-bottle, Fig. 87. It is a flat-bottomed glass flask, thin if to withstand heating, closed by a doubly perforated cork. Through one hole passes a glass tube A reaching nearly to the bottom of the flask and bent above to an angle of about 135°. Joined to the end of the bent limb by rubber tubing is a short tube B drawn down to a fine orifice, the flexible joint allowing the stream to be thrown in any direction. Through the other perforation a second tube C reaches just below the cork, and is bent to about 45° from the vertical. On blowing into D a fine jet of water is ejected from B.

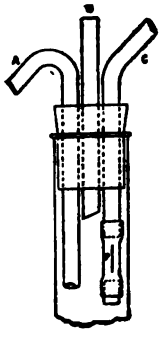

Fig. 88.

Two wash-bottles should be provided for general work, one for cold and one for hot distilled water. Others of smaller capacity for dilute hydrochloric acid, dilute ammonia, and a small one for the occasional use of the less common washing fluids, are not infrequently needed. To protect the hand the neck of the hot water flask is covered with some non-conductor like twine, chamois-skin, or cork. For dilute ammonia hydrogen sulfide and the like, the air pressure may be produced more pleasantly to the operator by the compression of a rubber bulb slipped over D or, as in Fig. 88, C may be terminated by a rubber tube the bottom of which is

plugged by a short glass rod; a longitudinal slit F between the rod and C forms a valve closing against external pressure; a third glass tube G, open at both ends, extends through the cork, and when the upper end is stopped by the finger and the air in the flask compressed by blowing into C, the stream of water continues until the finger is lifted.

For highly volatile liquids the tubes may be provided with stop-cocks or otherwise arranged to prevent evaporation. Corrosive or fuming liquids will soon destroy a cork or rubber stopper, and for these a bottle may be had made entirely of glass, the stopper ground in. Another form of wash bottle is simply a small flask with a cork through which passes a single tube drawn to a fine orifice; on grasping the bottle firmly and inverting, the air within, expanded by the heat of the hand, forces out a part of the liquid.

Where many precipitates are to be washed, a large bottle of water is set on a high shelf at the rear of the work table, and a syphon introduced, the outer limb entering a long rubber tube bearing a spring pinch-cock and terminating in a short piece of glass tubing with a small orifice. An elevation of the bottle three or four feet above the filter stand is sufficient to eject the water with considerable force.*

There are a number of devices for the automatic continuous washing of precipitates on the principle of the Mariotte bottle, as in Fig. 45. Generally speaking this method of percolation cannot be recommended for the reason that the precipitate receives no stirring and parts become less compacted through which the water descends preferentially, to the privation of the remainder.†

The operation of washing may be conducted either entirely by decantation as described, or after transferring the precipitate to the filter. Each way has certain merits and a combination of the two is usually resorted to in this manner; after filtering the clear supernatant liquid, the precipitate is roused with water (or other washing fluid), allowed to settle, and the liquid poured on the filter; repeating this one or more times, the precipitate is transferred by inverting the beaker over the funnel and washing out the sediment by a stream from the wash-bottle. Any particles adhering to the beaker so firmly that the stream will not remove them are dislodged by a short piece of black rubber tubing drawn over the end of a glass rod, or a conical tip of soft rubber fixed to a vulcanite rod (a "policeman").

The stream should be directed first around the funnel above the filter, then more forcibly into the precipitate to break up any channels formed, and at the final addition the precipitate is brought well down into the apex of the filter. It is obvious, considering the process as a course of successive dilution, that with a given amount of water the smaller the volume introduced at each washing the more thoroughly will the precipitate be cleansed, and for this reason each addition is made after the preceding one has quite run through. With a bulky precipitate it is well to allow a short time between successive washings that the adhering mother liquor may by diffusion become equally distributed throughout the precipitate.

Some precipitates have a fashion of creeping above the edge of the filter during the washing, then running down the exterior at its crease. This is prevented by *slightly* greasing the edge with pure vaseline; a funnel roughened interiorly by grinding is said to obviate this tendency.

Owing to evaporation the upper part of the filter becomes more charged with the soluble matter and care must be taken that it receives a due share of the wash water. If it is desired to limit the amount of wash water, after washing a few times the upper edge of the filter may be cut off, cut into pieces, and thrown in with the precipitate, and the washing completed.

The washings are usually allowed to flow into the beaker containing the filtrate. But should the precipitate be of such a nature that it tends to run

* Journ. Anal. App. Chem. 1893—126.

† Chem. News, 1892—2—55.

through the paper on washing, or if for any reason it is not judicious to expose the filtrate to the heat of evaporation in a subsequent concentration, the washings are collected separately from the filtrate.

A liquid residue or precipitate is washed in the same manner as a solid, but the filter is always to be kept partly filled with the wash water to prevent any of the liquid running through.

Successive portions of wash water are run through until an appropriate test shows that the attenuation has reached a point where the weight of the precipitate will not be sensibly augmented by the non-volatile impurities remaining, or that the chemical action of the remaining impurities that are volatilized on the ignition of the precipitate may be neglected.

The testing of the last washing may be done in several ways according to the nature of the impurities. As the final washing represents an extremely dilute solution it is always well to apply the test to a volume of several cubic centimeters rather than the few drops sometimes directed, as the indications are more apparent.

1. By observing whether a sensible residue is left on evaporation. This proceedure is of course invalid where the precipitate is not highly insoluble, or where the impurities are volatile on evaporation.

2. By the formation of a precipitate or coloration with a reagent. A little of the final washing is caught in a test-tube and examined for the precipitant or that compound that is present in the solution in the largest amount and presumably retained in the greatest proportion. Here it is essential that the qualitative test be a very delicate one, and it is best to view the mixed liquids vertically in a test tube as a change in color or a turbidity will be more plainly shown.

3. By some physical property, best observed on the predominating constituent of the solution. The rate of removal of a highly colored solution may be traced by the gradual lightening of the washings and also of the precipitate and filter paper, but it is always a safer plan to continue washing for a few times after the color has entirely disappeared. Some intensely sweet or bitter organic principles may be detected in highly dilute solutions by taste far more certainly than in any other way, but caution should be observed in tasting even dilute solutions of highly poisonous alkaloids or other bodies. And the removal of a substance having a pronounced or persistent odor is known by the washings becoming nearly odorless.

Occasionally a precipitate is met with that is stable and insoluble in the presence of some constituent of the solution in which it has been formed, but begins to decompose or dissolve when the constituent has been removed, or nearly so, by washing. The disappearance of the constituent in question from the washings or the appearance of the precipitate or a dissociation product therein is a warning to terminate the process; unless, of course, it is allowable that the constituent, another of the same character, or a dissociation product may be dissolved in the wash water.

When a precipitate on a filter is to be redissolved, an ample quantity of the solvent may be poured on it and returned when run through, until all is dissolved, after which the solution adhering to the filter is washed away. If the precipitate is bulky and one wishes to limit the amount of solvent, it is transferred to a beaker by a horn or platinum spatula, or, holding the funnel horizontally, washed out by a stream from the wash bottle; what remains adhering to the filter is dissolved by washing with the solvent, then with water. When the precipitate is to be dissolved in a moderately strong acid or alkali solution,

only the latter plan is feasible, as the paper would be broken were the solvent poured directly into the filter.

IGNITION — ROASTING.

Before proceeding to weigh a precipitate or residue it must be freed from moisture and brought to the state of a definite chemical compound if not already so. The water is removed by drying; the heat limited to 100° or below where volatile matter is contained that is not to be eliminated, otherwise by the temperature of melting or decomposition; though a volatile constituent m y be purposely expelled by heating should the remainder be more stable or have a less questionable composition than the original.

Drying. Precipitates wholly or in part decomposed or volatile at temperatures above 100° Cent. are dried in the water-oven. For holding the filter during the drying and weighing there can be used two watch-glasses of the same diameter bound together by a brass spring-clip, Fig. 81. The filter is folded and dried on one glass, then the other clamped to it and the whole cooled in the desiccator and weighed. A weighing-bottle of light glass, Fig. 84, is a convenient substitute for the watch-glasses. After the filtration and washing, the filter with the precipitate is dried, cooled, and weighed in the same way. The drying should be repeated until there is no further loss in weight.* For the comparatively few precipitates that are altered at a temperature below 100°, the heat is limited to a temperature as far below that where decomposition or volatilization begins as prudence dictates.

If it be feared that the fluid passing through will slightly dissolve and lessen the weight of the paper, or increase it (*e. g.*, barium hydrate is retained to a slight extent in spite of protracted washing), two filters from the same sheet are balanced by clipping their edges, put in funnels, and the filtrate from one passed through the other. After washing each separately and drying, one is placed on each pan of the balance, the difference in weight being that of the precipitate.

It is seldom necessary to protect a precipitate from oxidation or absorption of carbonic acid from the air during the desiccation, but if so, the drying tube, described on page 28, may be the container.

Ignition. The majority of inorganic precipitates can be heated to dull redness without fear of decomposition, fusion, or oxidation by the air. For practical reasons, ignition of a precipitate is usually preferred to the process of drying as described above, a choice of the two being allowed. The filter is burned and the precipitate heated to the proper temperature in a small crucible of metal or porcelain provided with a loosely fitting lid, and weighed therein.

Crucibles. Those made of platinum are rightly held in high esteem by the chemist for their many desirable qualities, and are always used in preference to those of other materials unless there are good reasons to the contrary. They may be heated and cooled rapidly without danger of fracture, withstand even a white heat for an indefinite time without softening or oxidation or any considerable alteration in weight, resist the solvent action of most chemicals, and are not brittle or easily injured. But certain reagents and fluxes cannot be heated in platinum without danger of corroding it and introducing platinum into the material contained; such are the sulfides of easily fusible metals, and their oxides, carbonates, sulfates, phosphates and arseniates when associated with carbon or organic compounds; free sulfur; baryta and the fixed caustic alkalies and their nitrates; and liquids containing or generating free chlorine or bro-

* Chem. News, 1892 -2—25.

mine. Metals fusible at the heat applied to the crucible will alloy with the platinum and perforate it.

Two shapes of platinum crucibles, Fig. 89, are manufactured, known as the tall and broad forms, the former being the standard shape and in general use. They range in capacity from 10 to 100 cubic centimeters, and weigh, including the cover, about as many grams as the volumes of water held. A crucible is made from a circle of heavy platinum foil spun into shape over a metal form leaving the crucible thicker at the bottom than at the edge. Some makers supplement the spinning by hammering the metal, which is claimed to compact it and diminish the tendency to superficial loosening or "blistering" under prolonged heating. The platinum used is the pure metal; an iridio-platinum alloy has been on the market for some years, much harder and stiffer than pure platinum and less liable to mechanical injury, and the manufacturers claim to have overcome its great defect, a tendency to crack during service.

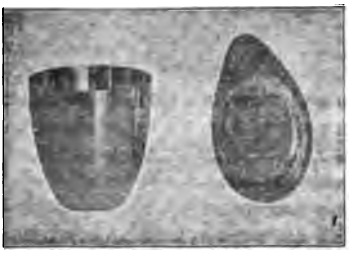

Fig. 89. $^1/_2$–$^1/_3$

A light crucible is quite as serviceable and long lived as a heavier one of the same size, given proper treatment. It has been advised that before putting a crucible into use, a mould be made by filling it with potassium bisulfate and melting over a Bunsen burner, that the original form can be restored if bent or bruised. However, the only occasion for distorting a crucible is for the removal of an obstinately adhering melt, and this difficulty may nearly always be obviated by certain precautions* (page 55).

Platinum vessels are cleansed after use by rubbing with moist, *water-worn* sand or precipitated silica. Refractory stains can be removed by digestion in strong hydrochloric acid or rubbing with sodium amalgam followed by water, or by melting sodium carbonate or potassium bisulfate in the crucible; these failing, as a last resort, treatment with boiling *aqua regia*.

A crucible of the usual tall form of a size holding about fifteen cubic centimeters of water will be found sufficiently large for most ordinary analyses.

A porcelain crucible, Fig. 90, is substituted where platinum would be injured by the substance heated therein, or a precipitate be reduced by the permeation of gases from the burner. They are made at the Royal Berlin and Meissen potteries of the finest grade of China clay, glazed inside and out. The sizes run from 5 to 300 cubic centimeters capacity. Their faults are fragility and liability to crack with sudden changes of temperature, and the difficulty of cleaning them after use, other than by hydrofluoric acid. The sizes best suited for general analytical work are Numbers 0 to 3.

Fig. 90. $^1/_1$–$^1/_4$

Silver and gold or gold lined† silver crucibles are used exclusively for fusions in which a caustic alkali or baryta is the flux; these metals are but little attacked by these chemicals as compared with platinum—gold less than silver—but have the disadvantage of softening and melting at much lower temperatures than platinum. Bunsen proposed to line the interior of a platinum crucible with a layer of mercuric oxide to prevent the corrosion following the ignition of certain sulphides.

* Crookes' Select Methods, 461.

† Chem. News, 1891–2–146.

Nickel, so exploited some years ago as a material for crucibles, has not fulfilled expectations, proving suitable only for oxidizations and ignitions at low temperatures and for fusions with alkalies.*

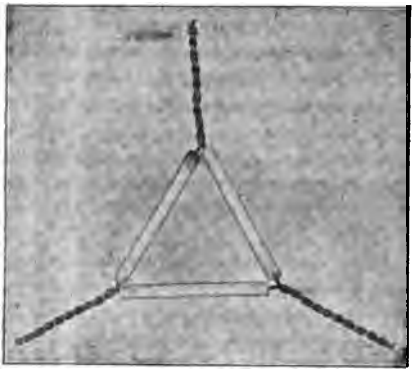

Fig. 91. 1/2

Appliances for ignition. The crucible is supported on a triangle made of platinum wire or iron wire wrapped with platinum foil or surrounded by pieces of pipe stem or clay tubes, Fig. 91, resting on the ring of an iron retort stand. The most convenient source of heat is the ordinary Bunsen burner, the air supply adjusted to give a perfectly non-luminous flame with the interior blue cone *sharply defined.* The bottom of the crucible should always be above the cone, since contact with it opens the polished surface of platinum to a canescent coating, also formed when the burner through faulty construction yields a large straggling flame. Should the flame be larger than is desired, a short glass tube fitting snugly in the tube and having the upper end slightly expanded may be inserted. The burner is shielded from draughts by surrounding it with a cylinder of fire clay about four inches in diameter, supported on three iron legs, the wire triangle resting on the upper edge of the cylinder.

Instead of a Bunsen burner, some prefer to conduct ignitions in a muffle heated to redness in a gas or coke furnace; a miniature muffle of platinum foil heated by Bunsen burners has been recommended for some technical work. The open crucibles are set just inside the front until the paper is burned, then gradually retreated to the hotter interior. From the radiated heat and free access of air, difficultly combustible forms of carbon, like graphite and dense coke, are more rapidly burned than over a free flame, and where a precipitate would be affected by reducing gases from a gas-flame permeating the hot platinum, or would absorb sulfur gases therefrom, a muffle is more suitable.

Blast-lamp. A temperature higher than that of a Bunsen is afforded by the blast-lamp, shown in Fig. 92, through the injection of a jet of air into the blaze at A. The gas enters at B, and the air at C. An extension sleeve D slides on E, and, when used in conjunction with the proper sized tip inserted in F, serves to adjust the flame from a fine point to a wide brush.

The compressed air is furnished by a foot bellows or by a fan driven by a water or electric motor. A water air-pump is shown in Fig. 93 delivering the air drawn in by a vacuum-pump (page 93). The waste-pipe from the pump A enters a metal cylinder B in which the air imprisoned in the waste-water is liberated, the water flowing away through the trap C. The air accumulating in B gives a moderate pressure and is connected at D by rubber tubing to C, Fig. 92.

For analytical purposes the blast-lamp is seldom needed, a powerful Bunsen burner meeting all the demands of ordinary work with a few exceptions.

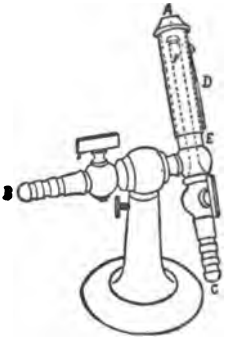

Fig. 92. 1/5

Igniting precipitates. The precipitate may be removed from the filter previous to ignition, but as this is not easily done without loss, it is better, unless

* *Chem. News*, 1887—1—11 *et seq.*

there are reasons to the contrary, to burn the paper with the precipitate inclosed. Most precipitates are not altered on ignition in contact with carbon, or but transiently; with these the filter and its contents are partly dried by opening it on several sheets of filter paper or a bisque clay plate. If the filter pump has been used in the filtration the effect of the pressure on the precipitate leaves it in a shrunken compact condition, so free from adhering water that it can be at once ignited without further drying, there being no danger of a projection of the precipitate or of cracking a porcelain crucible.

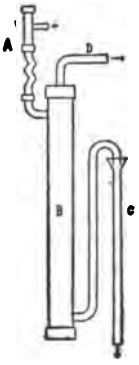

Fig. 93.

The filter is then folded around its contents and pressed into the weighed crucible. If a ring of precipitate is left in the funnel when the filter is withdrawn it is wiped out by a slip of filter paper also put into the crucible. The covered crucible is heated over a very low flame until no more smoke escapes, then turned on its side and the cover supported against the upper edge, Fig. 94; a piece of platinum foil laid under the front directs a current of air into the interior. When the char has burned (if necessary turned over occasionally by a thin platinum wire), the incrustation of carbon on the cover is dissipated by heating to redness; the crucible is turned upright, covered, and heated at the temperature and for the length of time specified in the method; transferred to a desiccator, and when quite cold is ready for weighing. If the crucible is weighed as soon as it has cooled, inclosure in a desiccator is not imperative, since only unweighable traces of moisture can enter the covered crucible in this short interval, though of course it is the safer procedure with compounds at all hygroscopic.

Fig. 94.

The above directions, however, will not apply to easily reducible metallic compounds, as a considerable weight may be lost from reduction or volatilization on ignition with carbon or reducing gases. With one of this character it is well to dry the filter by standing the funnel in the water-oven, and then remove the precipitate from the paper as completely as possible by rubbing the sides together over a sheet of glazed paper. After burning the filter to an ash in the tared crucible, the small amount of precipitate that has remained adhering to it is restored to the original composition by appropriate reagents (*e. g.*, when lead sulfate has been reduced to the sulfide or metal, a few drops of dilute nitric acid dissolves the residue to the nitrate, and a drop of sulfuric reprecipitates it; on evaporating the water and excess of acids, lead sulfate remains). The major portion of the precipitate is brushed into the crucible which is then heated to the proper temperature, cooled, and weighed.

Fig. 95. $^1/_5$

The crucible should be weighed empty before use as traces of platinum may

be dissolved when the precipitate is removed by a solvent; and if ignited over a blast-lamp, the weight should be taken both before and after the operation.*

Another way to burn the filter is to fold it compactly and wind around it the end of a thin platinum wire; the roll is kindled and held over the crucible, and when the flame has entirely died out, the char is burned to an ash by bringing a Bunsen flame near it, allowing the ashes to drop into the crucible. But slight draughts of air may easily cause mechanical losses.

The reduction of metallic compounds by carbon begins only at a fairly high temperature, hence if the heat of combustion be kept as low as possible, ordinarily but little or no reduction will take place. With some precipitates it may be the better plan to treat the washed precipitate on the filter with some volatile solvent and catch the solution running through in a tared platinum dish, then, after washing the filter, evaporate the solution plus washings, dry or ignite the residue and weigh. The solvent may be chosen to effect a simple solution only, the composition of the residue on evaporation being the same as that of the precipitate; or one that will change it to another definite combination, stable on evaporation and drying or ignition.

After filtration through a Gooch crucible by the aid of the vacuum pump, the precipitate is dried or ignited at once without transference. The Gooch is particularly well adapted for compounds of metals that are affected by carbon on ignition. For greater security against loss during ignition by reason of the finer particles of asbestos or the precipitate sifting through the holes in the crucible, a movable shoe, Fig. 81, may be fitted to the bottom, it being weighed as part of the crucible. The crucible and asbestos felt are to be heated before filtration up to the same temperature as will be employed in the subsequent ignition.

Burning filter paper. The physical character of the carbonaceous residue from cellulose heated in a closed crucible is determined by the degree of heat employed, varying from dull black, loose, and easily burned, to glossy, dense and refractory, and therefore the temperature in charring a filter should never rise so high that the escaping smoke will burn when touched with a flame. For incinerating the char, the under side of the crucible should be only dull red, air having free access to the interior, as at this moderate temperature the extent of the action of carbon on the precipitate is a minimum.

When a precipitate is slightly soluble in the fluid used for washing it, the pores of the paper remain impregnated with the solution, and the combustion is somewhat retarded, and the same effect will be noticed when the precipitate is of such a nature that during its ignition there is evolved a gas which is a non-supporter of combustion.

Filter ash. The weight of the ash of the filter is deducted from the total weight of the contents of the crucible. By burning a number of filters, say ten, in a crucible and weighing the total ash it is easy to compute the weight corresponding to a square centimeter of paper and to a filter of any given diameter. No deduction, however, need be made for paper which has previously been extracted by hydrochloric acid (page 90) or when an acid solution has been filtered through it, as the ash weight is here inconsiderable.

A liquid to be evaporated to dryness to obtain the weight of the solids contained is concentrated in a large dish to a small bulk, then transferred to a small tared capsule of platinum or porcelain and the evaporation completed. For evaporating concentrated solutions that are apt to spatter when heated directly over a Bunsen burner, Rogers has devised a special burner in which

* Caldwell, Chemical Anal. 128.

several small jets of flame are directed inwardly from a ring tube toward the upper part of a dish or crucible supported within the ring.

When a compound of gold, silver, or platinum with an organic radical is heated with free access of air, there is left a residue of the metal; organic compounds of barium, strontium, potassium and sodium leave carbonates; and other non-volatile metals remain as oxides. Ignition of such compounds should be carefully performed as the loose powder is apt to be carried away in the escaping gases. Salts which decrepitate on heating are first thoroughly dried on the water-bath and then exposed in a covered crucible to a very gentle heat over the burner until crackling ceases. It is advisable to inclose the crucible in a larger one, both covered, and weigh them together.

To convert into oxide a compound of an easily reducible metal with an organic radical, the compound is ignited with free access of air, the residue treated with a few drops of nitric or fuming nitric acid, evaporated, and again ignited. On heating the nitrates or chlorides of some metals, a small amount of the base is carried off in the escaping vapors; this does not occur with the sulfates, therefore it is well to add a slight excess of this acid to the solution before evaporation to dryness. The residue is heated either gently and weighed as sulphate, or more strongly to the oxide, according to the metal in combination.

Vegetable bodies contain alkali salts which tend to fuse and encyst the carbon and delay or entirely prevent complete combustion; moreover, if the heat exceed dull redness, or if a jet of oxygen be played over the surface to hasten the burning, there will be a liability of the volatilization of part of the alkalies. To meet these difficulties various plans of calcination have been proposed. Perhaps the one most used is that of first charring the substance at a very low heat, then lixiviating the soluble salts with water; the residual carbon burns easily, and to the inorganic residue is returned the aqueous solution, the whole evaporated to dryness, gently ignited, and weighed.

Another way of calcining vegetable substances is that of Fluckinger,* who, to prevent the material from burning with a flame, would calcine it in a platinum dish covered by a sheet of platinum gauze. When the volatile matter is expelled, the residue is treated with water, evaporated, and burned to an ash, this repeated if particles of carbon remain. Stone and Dickson,† in the determination of the ash of sugar syrups, aim to prevent the great swelling up in carbonization, unmanageable with large weights of syrup. They fill a small pipette with the syrup, weigh and hang over a small platinum dish kept at a red heat. The syrup is allowed to fall drop by drop into the dish, each drop carbonising before the succeeding one falls. When a sufficient quantity has been withdrawn the pipette is reweighed. The char is extracted by water and proceeded with as usual.

As the rapidity with which carbon is consumed depends largely on a free access of oxygen, in certain cases the particles of an organic substance in powder may be dispersed by the admixture of several times its bulk of some infusible inorganic powder, allowing the air to easily permeate the blend. The usual diluents for the purpose are magnesia, silica, precipitated silver, or some easily reducible metallic oxide; as all of these are insoluble in water, the soluble constituents of the ash may be lixiviated. For the absorption of certain products of the combustion of bodies containing acidogens, there may be added an alkali carbonate. This plan can be followed with safety in the determination of the ash of bodies that explode on heating.

Vegetable matter leaving a compact coke on strong heating may be diluted with one of these powders to advantage. Shuttleworth‡ would mix vegetable matter with a measured

* Zeits. Anal. 27—637.

† Journ. Anal. Appl. Chem. 1893—319.

‡ Analyst, 1899—271.

volume of a solution of calcium acetate of known concentration, then evaporate to dryness; the calcium oxide, formed from the acetate when the mixture is ignited, not only hastens combustion but makes the ash more refractory. The weight of extrinsic lime in the ash is calculated from the volume of the solution of calcium acetate.

Another plan is that of moistening with a solution of some organic compound that is volatile at a moderate heat, such as benzoic acid; on evaporation and ignition the vapors evolved cause the residue to swell and become spongy and easier of combustion.

Some organic bodies burn readily and completely when moistened with strong nitric acid, dried, and ignited, at first gently, then to full redness. A probable alteration of the composition of the ash must be considered, however.

On igniting a complex substance in the air, the inorganic residue may not be left of the same composition as in the original, being decomposed by heat alone, oxidation by the air, or reduction by carbon, or by two or all of these.

For example, the ash of vegetable matter is largely in the form of carbonates of the alkalies and earths, resulting from the combustion of the original organic salts. In reporting results some analysts deduct the carbon dioxide and return the remainder (oxides) as the ash; others attempt, often with doubtful warrant, to compute the original composition from an analysis of the ash. Where the inorganic bases have been converted to sulfates by evaporation with sulfuric acid, the result is reported as "sulfated ash," or a conventional deduction is made for the sulfuryl. Sometimes the residue may be reconverted to the original composition by treatment with appropriate reagents, evaporation, and drying at a low temperature.

Although it may be said that the majority of precipitates are weighed in the same chemical combination as thrown down from solutions yet exceptions are numerous. The precipitate may be of a somewhat indefinite composition or contain another body admixed in indefinite proportion; or the composition is changed in part or entirely to another by the action of the heat of drying or ignition to volatilize some constituent or produce an inter-reaction, by the reducing effect of carbon or the pyrogens of the filter paper, by oxidation by the air, or from the action of aqueous vapor or carbon dioxide. Precipitates or residues from evaporation or partial solution, of the nature described above, are brought to a combination suitable for weighing in the following ways:—

1. By heat alone. Some one volatile constituent is expelled, proportionally reducing the molecular weight, or extrinsic volatile matter mixed with the precipitate is driven out. The change in composition is usually indicated by some physical alteration of the precipitate. That a definite compound results is more certain if the change in composition is induced only at a high temperature; if at one more moderate, it is essential that no further alteration will occur should the heat be increased.

By ignition, a higher oxide or a mixture of several higher oxides may be brought to one definite stable lower oxide, oxygen escaping; some per-salts are changed to proto-salts; ammonium salts with volatile radicals, loose-bound halogens, free sulfur, and carbon dioxide pass off as such; inorganic bases combined with organic radicals, and many sulfates and nitrates are decomposed, leaving residues of carbonates or oxides; etc. In most cases the original composition can be restored by moistening the residue with a solution of a reagent wholly volatile containing the element or radical driven off, then gently igniting; *e. g.*, calcium carbonate on intense ignition passes to calcium oxide, but on moistening the oxide with a saturated solution of ammonium carbonate, it is reconverted to the carbonate.

The water of constitution of stable bodies is usually determined by igniting the substance in a closed platinum crucible. The loss in weight is assumed to be combined water only, but may include other volatile constituents and easily

combustible carbonaceous matter; moreover, the composition of the residue may have undergone a change by internal reactions, oxidation by the air or aqueous vapor, etc.

A direct determination of combined water is always advisable where the composition of the material in hand is not known with certainty. The apparatus is a long porcelain combustion tube laid horizontally in a combustion furnace (page 296) and connected at one end to a source of dry air, and at the other to a weighed U-tube containing dried calcium chloride. The substance is dried at 100 ° and a suitable amount weighed in a porcelain boat; the boat is inserted midway in the tube and the latter connected up air-tight with the U-tube. A slow current of dried air is passed through the train while the porcelain tube is heated about the middle to bright redness. The U-tube is detached, cooled and weighed, the increase being the water expelled from the substance. Hygroscopic moisture may also be determined in the same way by subjecting the undried substance to the above process and taking the difference between the two results.

For a direct determination of the water of minerals, Brush and Penfield* prepare a tube of hard glass with a bulb A at one end and two bulbs BB about the middle. The mineral is placed in A, and BB cooled by wet paper. On heating the mineral, the water distills and condenses in BB; the tube is then drawn off by a blowpipe flame near A, cooled and weighed. The water is poured out, the tube dried and reweighed. A short rubber tube drawn over the end of a glass rod serves as a stopper for the tube during the weighings.

2. By oxidation to a higher compound. Various suboxides on ignition in the air pass to a stable higher oxide, though it is the safer plan to supplement the operation by treatment with a more energetic oxidizer than the air, such as pure oxygen, nitric acid, or bromine water. A fairly large platinum crucible will answer, but to maintain a uniform heat throughout the mass, it is better that the crucible be inclosed or suspended within a larger one of platinum or porcelain, thus heating the inner one by radiation only.

Most metallic sulfides and sulfo-salts on ignition in a current of air are transformed eventually to oxides, sulphur dioxide escaping. Moderate heating at the beginning of the process is here of prime importance, since the sulfide may sinter or even fuse at a dull red heat, and the oxidation proceed very slowly. After partial conversion at the lowest temperature practicable, the flame is cautiously raised, finally heating to bright redness. Mercuric oxide, volatile at a red heat, may be mixed with the sulfide to assist oxidation, or a weighed amount of some stable metallic oxide in fine powder to act as a carrier of oxygen.

3. By reduction to a lower oxide or other condition. The reduction may be done by means of some reducing gas, usually hydrogen, carbon monoxide, or the vapor of formic acid,† in a porcelain or platinum crucible. The gas is passed in through a bent porcelain tube, bearing a shield to serve as a loose cover. The current of gas should be slow, and it is safer to interpose a disk of perforated platinum between the precipitate and the end of the tube to prevent mechanical loss. The apparatus is also of use in ignitions where it is desired to protect sulfides from oxidation by the air. Hydrogen and other gases highly compressed in steel or copper tanks or steel cylinders are now on the market, the gases guaranteed of a purity sufficient for this and like purposes.

4. By transformation to another combination; as where the acid radical is exchanged for another. The most common is the conversion to the sulfate of

* Amer. Journ. Science, 1894—31.

† Analyst, 1898—16.

a compound of a base with a volatile acid radical by evaporation with a slight excess of sulfuric acid followed by gentle ignition. Less often is a compound converted to the chloride. If the freed radical is not volatile and the sulfate or chloride is insoluble, the former may be removed by lixiviation, but in this case it is the better plan to redissolve the precipitate before drying and reprecipitate in a weighable combination.

Sometimes a precipitate or residue is obtained in analysis consisting of a definite compound $a\,b$ mixed with an indeterminate amount of the same base or acid b that exists in the compound—thus magnesium borate with magnesia. Usually the simplest procedure is to find the weight of the mixture and then determine the total base or acid radical, easiest by conversion of the entire base or acid to a definite compound; the difference is a from which the base or radical combined with it may be calculated.

That a dried or ignited precipitate contains impurities to a ponderable extent may be evidenced by an abnormal color or agglomeration, fusibility at a lower heat than should melt the pure compound, an escape of fume on heating, or condensation of sublimed matter on the bottom of the crucible lid, and other characteristics.

In all cases it is the part of prudence to test the weighed precipitate to make sure that it is one definite chemical compound and free from other bodies. The method of examination is decided by the nature of the compound and the impurities likely to contaminate it.

1. Lixiviation with water or other liquid in which the precipitate is insoluble, followed by evaporation or precipitation. Soluble impurities are detected in this way, sometimes apparent in the lixiviation by color or taste. But often the impurities are, in large part or wholly, so inclosed in or attached to the precipitate as to resist solution; in this case they may usually be freed by effecting some structural or chemical change in the precipitate, *e. g.*, an oxide reduced to metallic powder by ignition in a reducing gas, or a metal oxidized by ignition in oxygen.

2. The precipitate may itself be dissolved, leaving the impurities as such or changed to an insoluble form by reaction with the solvent. This scheme, though less often available, is generally preferable to the above, as the impurities, forming only a small fraction of the precipitate, are left reasonably pure, and may be weighed and deducted from the combined weight.

3. Both the precipitate and the impurities may be dissolved by a suitable solvent, and a reagent introduced in the solution that will precipitate only the former; the impurities can then be tested for in the filtrate, or may sometimes be evidenced by the color of the liquid.

4. Both the precipitate and impurities may be transformed to another combination and the resulting mixture weighed; this weight should equal that calculated by stoichiometrical rules, any discrepancy being credited to the presence of impurities. For example, calcium oxide on evaporation with sulfuric acid leaves calcium sulfate weighing 2.43 times that of the oxide. Any associated barium carbonate would pass to barium sulfate weighing only 1.18 times that of the carbonate; and any silica present would retain its original weight.

Similarly, a precipitate may be evaporated with the same volatile acid as forms the radical of the compound, when, of course, the weight of the pure precipitate will remain unchanged, but that of the impurities of a different composition may be more or less altered. However, these methods are only of

use in a few special cases, as the variation in the total weight is usually so small as to make it doubtful whether it should not be ascribed to other causes

5. Various special tests will be suggested to the operator during analysis, equal or superior to those outlined above.

CHAPTER 5.

VOLUMETRIC ANALYSIS.

In volumetric analysis the weight of a body is determined by finding what weight of a given reagent is requisite to exactly fulfill the reaction taking place between them. In practice there is used a 'standard solution' of the reagent — an aqueous solution whose concentration has been accurately ascertained. The usual routine is to weigh a suitable amount of the substance in which the proportion of the constituent body is to be determined, dissolve in water or other solvent (forming the *titrate*), and gradually run in the standard solution (the *titrand*) until the reaction is complete, this point being manifested by the incipience of a secondary reaction or otherwise. The weight of the substance, the volume of the standard solution, and the combining weights as shown by the equation describing the reaction are the data for computing the result.

The reactions on which depend the methods of volumetry may be classified as follows: —

A. The combination of acids with alkalies or earths: as sulfuric acid neutralized by ammonia; calcium hydrate by oxalic acid.

B. An increase or reduction in the number of atoms in a molecule: as stannous chloride perduced to stannic chloride by ferric chloride; ferric chloride reduced to ferrous chloride by stannous chloride.

C. A change in the acid radical combined with a base or vice versa, the new compound usually insoluble: as barium nitrate converted to barium sulfate by sulfuric acid; sodium chloride to silver chloride by silver nitrate.

D. A direct union of the molecules of the titrand and titrate: as anilin with chloroplatinic acid, giving anilin chloroplatinate.

E. A few reactions of special application are not included in the above.

Apparatus for measuring. As gravimetric analysis is founded on the determination of mass by exact weighing, so the basis of the practice of volumetric analysis is the accurate measurement of liquids. For this purpose there are employed glass instruments of four varieties, namely *measuring* or *volumetric flasks*, and *graduated cylinders* or *measuring jars* to contain, and *burettes* and *pipettes* to deliver certain volumes of liquids. The height of the surface of a liquid of a given volume is indicated by a horizontal line etched in the glass.

The unit of capacity under the Metric system is the cubic centimeter — the volume of one gram of pure water weighed in vacuo at the sea-level and at the temperature of its greatest density, 4° Cent. — therefore, following Fresenius, all the vessels intended for volumetric purposes should contain or deliver, as the case may be, the specified number of cubic centimeters weighed at this temperature.

But Mohr advanced the objection to this rule that at the ordinary temperature of the laboratory it is impossible to graduate or confirm the graduations by weighing, on account of the deposition of dew on the exterior of vessels con-

taining water at 4°, and proposed that the volume of one gram of water weighed at 17.5° should constitute the unit for the purpose. The precedent has encouraged the advocacy of other arbitrary temperatures, such as 15°, 16°, 20°, and 25°, resulting in a multiplicity of standards, with attendant confusion and liability to error. While the actual content of the different instruments one has in use is seldom a matter of consequence provided all are based on one standard, the proposal to depart from the rational standard of 4° was unfortunate since neither accuracy nor convenience (the coefficients of the expansion of water by heat being exactly known) is enhanced, and the significance of the term 'cubic centimeter', which should be reserved for a definite invariable volume, and any other volume given a distinguishing name, is made ambiguous.

In selecting an outfit of volumetric ware one must make sure that the temperature at which they were graduated was the same for all. The importance of this provision will be seen when it is considered that 1000 cubic centimeters of water at 4° Centigrade expands to 1000.85 Cc. at 15°, to 1001.73 Cc. at 20°, and to 1002.87 Cc. at 25°. In the United States the temperature of 15° has been generally adopted.

The "Mohr" of DeKoninck is 1000 "fluid grams", a fluid gram or "millimohr" being the volume of a quantity of water at 15° of which the weight determined in the air at 15° and under a pressure of 760 millimeters of mercury, by means of brass weights, is one gram.

The *burette* is an open glass tube supported vertically, from which any desired volume of liquid within its capacity may be poured, or, in the more recent forms, drawn from the bottom through a tap with a small orifice. The usual sizes are from one-fourth to three-fourths of an inch in internal diameter, delivering a total volume of 30, 50, or 100 cubic centimeters, graduated into cubic centimeters and fifths or tenths of each.

Various devices to control the outflow are in use, a choice depending largely on personal fancy and all having some objectionable features for practical work.

Of the styles delivering their contents from the top, Binks', Gay-Lussac's, and Casamajor's, are simply different forms of a slender measuring-jar set in a broad metal or wooden foot, the solution poured out in a stream or by drops as desired. In Casamajor's the tube is held nearly horizontal, the base resting on a block, and rotated so far to allow the solution to flow from a curved spout; Gay-Lussac's is fitted up with tubes like a wash-bottle, an improved form having the longer branch of the exit tube inclosed in the burette. Several defects are inherent to all burettes of this style and they have been very largely supplanted by others such as are described below.

Among the forms of tap that have been invented for burettes delivering the liquid from below, that of Mohr, Fig. 96, is in common use. The lower end of the burette is contracted to a smaller bore and joined by rubber tubing to a narrow glass tube drawn to a small orifice. A spring pinchcock compresses the rubber tube so tightly that no liquid can pass, and can be opened at will by pressing the disks, allowing a stream of any desired speed to flow. Instead of the pinchcock, a short glass rod of the same diameter as the interior of the rubber tube may be held within it; when the rubber tube is compressed between the thumb and finger, two narrow channels are opened. The burette is partly filled with the titrand by first inserting the orifice in the liquid, opening the pinchcock, and applying suction at the top until the liquid has risen above the tap; after this the titrand is poured into the burette. Proceeding in this way avoids the danger of entrapping air bubbles in the tap.

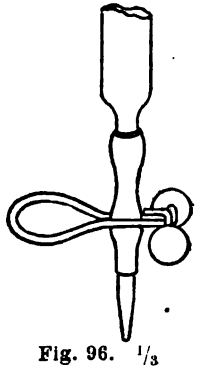

Fig. 96. 1/3

In Koenig's design, Fig. 97A, the lower end is contracted and cut off obliquely. The orifice is closed by a platinum or rubber plate A ground to fit, which is pivoted to a brass spring S that presses the plate against the glass. The pressure of the spring is released on turning the screw T.

Winkler's burette is shown in Fig. 97B. Within the burette and extending to the bottom is a rod of heavy glass, the lower end drawn to a cone and ground to make a water-tight valve with the contraction of the burette at that point. The upper end is supported in a frame and slightly lifted from its seat by a simple mechanism under easy control of the operator.

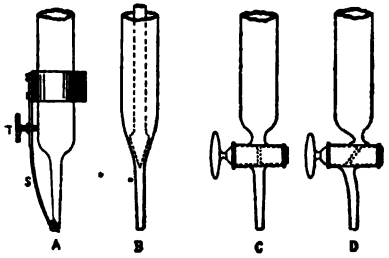

Fig. 97.

Carbutt describes a peculiar design of burette for which several advantages are claimed. The reservoir of the titrand is a closed flask from which the liquid is drawn by a syphon tube, and as the titrand leaves the flask an equal volume of air must enter. Not the volume of liquid withdrawn is measured, but that of the air replacing it, this ascertained by a water-manometer connected with the flask.

All things considered, probably the most generally serviceable form is that shown in C, the tap a ground-in glass stopcock, it having the advantage, among others, that solutions slowly decomposed by rubber can be used in any concentration. The plug of the stopcock should be well fitted so as to turn smoothly without sticking at any point, and when slightly lubricated with vaseline,* allow no leakage. The oblique-bore stopcock D, introduced by Greiner, is an improvement on the older form, as in the latter a groove may be worn in the socket by the edges of the perforation, allowing liquid to pass.

It is much more convenient for most operators that the handle of the plug be situated at the left hand when facing the graduations than at the right as is usual. The plug should be withdrawn and tied to the burette before putting away the latter; if this is not done the plug may later be found cemented in the socket, especially after the use of caustic solutions. In cold weather the stopcock should not be left closed over night, as the plug is invariably split when the liquid in the bore freezes.

When a number of titrations are to be made with the same solution, the burette can be arranged to connect by glass and rubber tubing with an elevated reservoir, so that by simply opening a pinch-cock the burette fills. The tubing should not be of rubber for titrands affected by this material, nor, according to Greiner, for reducing solutions, as oxygen from the air will pass through and oxidize the solution. Another scheme is that of substituting an oblique three-way stopcock for the straight-way plug; when the plug is turned 180° from the position shown in Fig. 98, the solution enters the burette from a rubber tube slipped over the side tube, while at 90° both communications are closed.

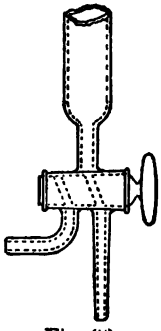
Fig. 98.

In a device described by Greiner, Fig. 99, the lower end of a narrow tube A enters a Woolf's bottle containing the titrand. By suction on a rubber tube connected to B the titrand is drawn up through A into the burette to above the zero mark; on allowing air to enter B there recedes into the bottle all above the orifice of A. As this point is the zero of the graduation, the titration may be at once proceeded with.

Whatever style of burette be preferred, a perfect instrument must meet two important requirements, namely that the outflow be under perfect control of the operator, that he may be able to withdraw the titrand in a full stream or by drops, as desired, and that when the tap is closed there is no leakage whatever.

* Journ. Amer. Chem. Socy. 1898—679.

As a rule, the taps of burettes found on the market have too large orifices, making it difficult to withdraw a small drop; moreover, no time is saved in a titration by the larger stream, since a proportionately longer period must be allowed for the liquid to collect from the sides of the burette before reading the volume withdrawn. When the outflow exceeds a rate of one cubic centimeter per second, the opening should be reduced by carefully heating the tip in the flame of a Bunsen burner, while constantly rotating it.

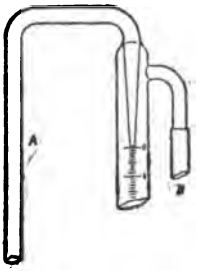

Fig. 99.

When not in use, burettes should be kept filled with some fluid which will keep the interior chemically clean, such as concentrated sulfuric acid for those entirely of glass, and a weak solution of chromic acid for the other forms. A film of grease is easiest removed by rinsing with a strong solution of caustic potash in alcohol or allowing to stand for some time filled with a concentrated solution of potassium permanganate, then rinsing with strong hydrochloric acid. When a volumetric solution is to be left in a burette for any length of time the top should be stopped by a cork or capped by an inverted test-tube, to prevent evaporation and the entrance of dust and fumes. Absorption of acid fumes from the air by caustic alkali solutions is guarded against by a cork bearing a tube filled with soda-lime.

Reading. After rinsing with the solution it is to contain, the burette is filled to above the zero mark, the funnel removed, and the tap opened until the bottom of the meniscus in transparent and the surface in opaque solutions coincides with the zero mark. With opaque solutions the exact height may be read without difficulty, but with the lighter colored liquids the double line at the meniscus, most apparent when the light falls from certain directions, is somewhat confusing, and various ways have been devised to secure a sharper definition.*

1. A card, the upper half white and the lower half painted a lusterless black, is held behind the burette at such a height that the line of junction of the black and white is one or two divisions below the meniscus; the reflection of the black surface in the meniscus shows as a black line sharply defined.

2. A light glass buoy (Erdmann's or Beutell's float, Fig. 100), weighted with mercury so that it remains half immersed, and circumscribed with a line coinciding with the division to be read; the best form of Erdmann's float is provided with six blunt protuberences of glass in order that it may quickly rise through the liquid when submerged. Or a disk of hard paraffin, one or two millimeters thick and of slightly less diameter than the interior of the burette may float on the surface.

Fig 100. $^2/_3$

3. The Shellbach burette has inserted at the back a stripe of blue glass bordered by white, the combination producing at the surface of the solution the appearance shown in Fig. 101; the graduation mark directly in front of the junction of the apices is read.

4. Carnegie proposes to deposit a mirror of silver on the back of the burette by means of a silvering solution. The graduation marks are made to reflect more distinctly by rubbing into them a paste of mercuric iodide in turpentine.

* Chem. News, 1895—1—43; Journ. Amer. Chem. Socy. 1899—42.

5. The simplest method and one quite satisfactory, is to rest the burette-stand on a window-sill and read with the eye aligned with the bottom of the meniscus and a horizontal line on some far distant object, such as the window-cap of a house.

Fig. 101.

Whatever plan be adopted, the eye should always be at the level of the point of reading. In the instruments of the German Physical-technical Institute the lines of the macro-divisions are produced entirely round the burette, the sub-divisions half round.

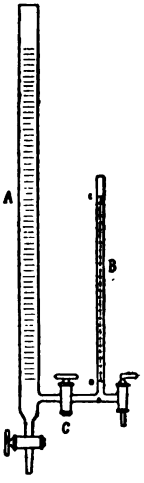

Fig. 102.

The narrower the burette, the more easy to read by reason of the greater space between the lines marking the fractions of the cubic centimeter, yet for technical work a burette longer than about 30 inches stands too high above the table for convenience in filling and drawing off the titrand to the zero mark. If it is deemed necessary to read the volumes withdrawn to closer than one-tenth of a cubic centimeter some special modification of the burette may be adopted.

Meinicke's burette, Fig. 102, has two branches connected by a stop-cock; the burette proper, A, holds 60 Cc. and is divided in units only, while the narrower branch, B, holds but one Cc. and is divided from the bottom upward into hundredths. The titration is done from A, the liquid in B standing at zero. If, at the end of the titration, the titrand is not exactly at some one division, the stopcock C is opened until this occurs, when the volume delivered is the difference between the readings of the two branches.

Some chemists prefer to weigh the titrand rather than to measure it, and for this purpose variously shaped glass vessels have been designed, compact in construction to admit of suspension within the pan-wire of a balance, or to stand on the pan. One of these is illustrated in Fig. 103. It is a short inverted burette, A, fitted at B with a tap, fused into the mouth of a flask, C, having a lateral branch, D. The flask is partly filled with the titrand and the burette filled from the flask by air pressure at D. The flask is then weighed and fixed in an inverted position in the clamp of a retort-stand; the titration is performed as usual and the flask is reweighed. The burette is graduated for convenience in drawing out nearly the volume of titrand required when this is approximately known.

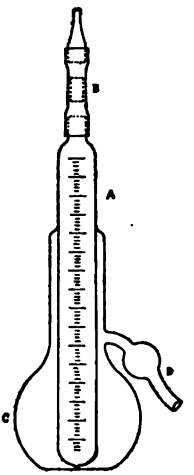

Fig. 10

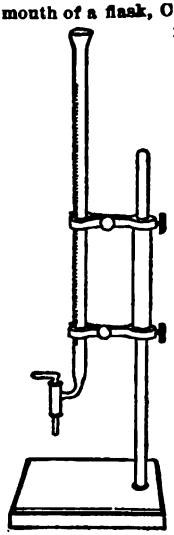

Fig. 104.

The burette is held vertically in the screw-clamp of a stand, Fig. 104, usually made of hard wood throughout, the clamp sliding on the post and fixed at a suitable height by a set-screw. On the base is placed a sheet of white paper or a glazed white porcelain plate to show plainly a slight change in color of the titrate. Wooden stands can be given a permanent white coating by painting with acid-proof enamel.

Chaddock's burette stand has a wooden base in which is inlaid a disk of opal glass; from a post rising at the rear of the base project heavy brass wires that have been bent to such forms as will spring together with sufficient force to hold the burette at any height by friction alone. Advantages claimed are the ease of removal and replacement of the burettes, simplicity of construction and cheapness.

Where several burettes are in occasional use, each reserved for a special solution, a

rotary stand has the advantage of taking up but little room on the work-table. From the center of a circular porcelain plate rises a brass rod carrying a slide provided with eight radial arms. Each arm has a clamp at the extremity for holding a burette or pipette; the slide may be rotated to bring any burette to the front.

Pipettes, Fig. 105, are calibrated to deliver certain volumes of a liquid, the usual sizes having a capacity of 1, 2, 5, 10, 25, 50, 100 and 200 Cc. The construction is that of a cylindrical bulb terminated by narrow open tubes, the lower one contracted to a small orifice, the upper circumscribed with a line from which the specified volume is delivered. In the smaller sizes the lower tube may be left off, the bulb narrowed to the proper sized orifice. For volumes not exceeding ten Cc. they are also made in a tubular form and graduated like a burette to deliver fractions of a cubic centimeter.

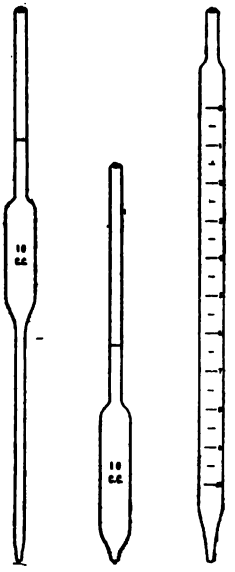

Fig. 105. 1/4

The measurements from a pipette are somewhat more accurate than from a burette on account of the smaller diameter of the tube at the line of calibration. The orifice should be so small that not less than about 30 seconds is required for the outflow; if too large it should be contracted by heating in a Bunsen flame, but the pipette must afterward be restandardized since the amount of liquid adhering to the interior varies with the rapidity of the outflow.

The pipette is held between the thumb and second finger and the solution drawn in by suction to an inch or more above the mark; then loosely stopping the top with the forefinger as shown in Fig. 106, allowed to run out until the bottom of the meniscus is on a level with the mark. The finger is then pressed down firmly and the pipette held vertically over the receiving vessel. After discharging the contents, one minute is allowed for draining, and the orifice is touched to the surface of the liquid to disengage the remaining drop uniformly though only partially.

Fig. 107

Only by adopting some one rule in dealing with the afterflow in the graduation and in practice, will the proper volume be delivered. The one just stated is sanctioned by most authorities, though others prefer either to remove the pipette as soon as the flow has ceased, to blow out the remaining drop, or to keep the orifice immersed while the pipette is emptying. For normal pipettes of their certification, the Deutsche Physicalisch-technische Reichsanstalt directs that the outlet be held against the wall of the receiving vessel, and when the flow has ceased to allow fifteen seconds for draining.

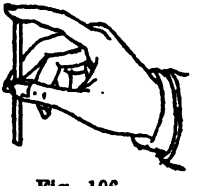
Fig. 106.

A pipette is calibrated for the delivery of the specified volume of pure water, a certain small part of the contents remaining on the walls. For dilute aqueous solutions of inorganic bodies the difference between the volume retained and that of pure water is practically inconsiderable. But for concentrated solutions and some dilute solutions of organic matter in

water, and for liquids like alcohol and ether, the volume adhering is greater or less than of water, and the volume delivered must be corrected where accuracy is important, or the pipette recalibrated for the particular liquid or solution measured. Some analyses call for two or more equal volumes of an alcoholic or ethereal solution approximating a round number of cubic centimeters, and here a uniform delivery is had by permitting a certain arbitrary number of drops — from two to ten — to fall after the flow has ceased.

In dealing with a liquid evolving a poisonous or offensive gas it is well to interpose between the pipette and mouth a tube packed with cotton that has been moistened with water or some absorbing chemical solution. But if the proportion of a gas in the solution is to be determined, it is advisable to weigh the solution rather than measure it out from a pipette, as with the latter there is a slight loss in drawing in the liquid from the reduction of the air pressure. Special pipettes are for sale adapted for measuring highly corrosive and fuming liquids.

The 100 cubic centimeter pipette used to measure the sodium chloride solution in the volumetric assay of silver alloys differs somewhat in form from the ordinary pipette, in order to secure greater convenience and accurate measuring. As illustrated in Fig. 107, the upper tube is contracted to a small orifice, and the pipette filled by gravity from an elevated reservoir containing the standard salt solution. The two are connected by a rubber tube, D, the flow being regulated by a pinchcock. As soon as the solution overflows into the waste-cup E the orifice F is stopped by the finger, the pinchcock closed, and the rubber tube removed. The exterior is wiped dry, and on removing the finger the entire contents (100 Cc.) flow out.

Fig. 109.

A modification of the above is shown in Fig. 108. At the bottom is a three-way stopcock; turned in one direction it allows the pipette to fill to overflowing, and in the opposite direction delivers the specified volume.*

A convenient form of pipette for delivering a number of equal volumes of a liquid is shown in Fig. 109.†

In technical work dealing with a liquid of constant density a special pipette may be provided which is calibrated to deliver a certain weight of the specific liquid, usually a round figure. Should the specific gravity of different samples of the liquid vary somewhat from the normal or average, the pipette may be graduated so as to bear a mark corresponding to each degree of gravity for some distance above and below the average. To save calculations, pipettes can also be ordered of a capacity to deliver a certain weight of one particular liquid — *e. g.*, milk, sap, vinegar — of fairly constant gravity, an amount suitable for the analysis. Though less accurate than weighing, the approximation is near enough for practical purposes.

Fig. 108.

Or, if a certain weight of a solid or liquid is to be dissolved in a solvent, then make up to a fixed volume and an aliquot part withdrawn for analysis, for any one constituent may be provided a special pipette that shall deliver exactly the same number of cubic centimeters as the percentage of the element to be determined is contained in the compound weighed, or some multiple or fraction thereof.

Thus, in dealing with a mixture containing X per cent of a constituent c; a weight a of the mixture is dissolved and the solution made up to a volume V; from V is drawn out an aliquot part v, and the constituent c precipitated from it as the compound cr that is found to weigh d grams and contains p per cent of c. Then, $X = \frac{Vdp}{va}$. Now if v be made to

* Analyst, 1898—279; Chem. News, 1892—1—63.

† Chem. News, 1992—1—125; Analyst, 1898—55 and 223.

equal p, then $X = \frac{Vd}{a}$; or if v be made to equal $\frac{p}{a}$, then $X = Vd$; or if v be made to equal $\frac{Vp}{am}$, then $X = m.d$; for m selecting any suitable number.

Measuring flasks, Fig. 110, are calibrated to hold accurately a round number of cubic centimeters at a given temperature, to the line A encircling the neck. A second mark is sometimes provided from which the specified volume may be *poured*, the difference between the two being a volume equal to that of the liquid remaining adherent to the interior of the flask; a pipette is more suitable for this purpose, however. Each flask should have a narrow neck closed with a well fitting glass stopper or a sound cork, and a sufficient space left above the mark to permit thorough mixing of the contents. The sizes grade from 25 to 2,000 cubic centimeters capacity. The glass should be well annealed to allow the boiling of a solution if desired.

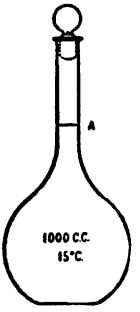

Fig. 110. 1/8

Giles' liter flask* has a bulb in the neck above the mark and a second mark at 1100 Cc. It is designed for the making up of standard volumetric solutions, allowing 100 Cc. to be withdrawn for standardizing, and leaving an entire liter of solution for practical use.

Measuring jars, Fig. 111, open at the top with a lip for pouring, or closed with a glass stopper, are of various capacities, the sizes running from 10 to 1000 cubic centimeters. The graduation is in whole cubic centimeters or fractions thereof, according to the size of the jar, and is usually marked on one side taking the bottom of the jar as zero, and on the other down from the top line taken as zero. Their comparatively large diameter unfits them for close measurements, yet they are very convenient where this is not essential. It is directed that normal measuring jars be emptied by reversing and allowing them to drip for one minute; then the adhering last drop is taken off with a glass rod.

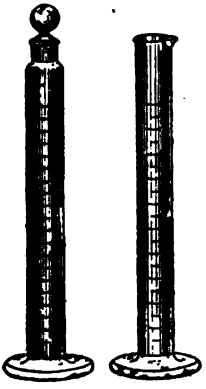
Fig. 111.

For general work the following assortment of glassware will be found sufficient: a burette of 50 or 100 Cc., measuring flasks of 100, 250, 500, and 1000, pipettes of 10, 25, 50, and 100, and jars of 10,50, 100 and 1000 Cc. capacity.

The end-point of a titration is shown by some visible physical alteration in the titrate or a portion of it. The change is sharply marked and easily discernible in all commendable methods and may be manifested in several ways.

A. By the cessation of precipitation. When a solution of lead chloride is titrated by a solution of potassium chromate there falls a precipitate of lead chromate; the titrand is run in until the last drop produces no turbidity in the clear liquid above the lead chromate which rapidly subsides.

Again, in the titration of methylamine by oenanthol, both dissolved in benzene, one of the products of the reaction is water — $CH_3.NH_2$ (methylamine) + $C_6H_{12}COH$ (oenanthol) = $C_6H_{12}.CH_3NOH$ (methylamine-oenantholylene) + H_2O. Previous to the titration there is mixed with the titrate some fused

* Chem. News, 1894—1—99.

calcium chloride; as the titrand is run in a cloud appears from the separation of water (immiscible with benzene). But the water is quickly absorbed by the calcium chloride on stirring, and the titrate becomes clear, allowing the end-point to be easily observed.

The possibility of distinguishing the end-point in titrations of this kind is determined by the physical character of the precipitate and its gravity as compared with the liquid in which it is formed. Most precipitates settle or clot so slowly that a small portion of the titrate must be filtered off after each addition of the titrand, and the filtrate tested by the titrand or another reagent. Various forms of miniature filtering apparatus have been brought forward for the purpose.

One of these is simply a short glass tube, the lower end tightly plugged with cotton and dipped into the solution. Suction is applied to the open end, and when a few drops of clear fluid have entered, the tube is removed and inverted over a test-tube. Another plan is to immerse the apex of a small paper filter beneath the surface of the solution; a little of the liquid passes into the interior and can be withdrawn by a small pipette or medicine dropper.*

B. Conversely, by the complete solution of an already formed precipitate. When (insoluble) mercuric ammonium chloride suspended in water is titrated by potassium cyanide solution, a soluble double salt is formed and the precipitate is gradually taken up by the water until at the end-point the last trace of opalescence disappears. The success of a titration of this kind depends, of course, on the readiness with which the precipitate is transformed to the soluble combination, and its insolubility in the products of the reaction.

C. By the formation of a precipitate in a clear solution through the decomposition of an already formed soluble complex. Thus potassium cyanide titrated by silver nitrate; there is formed soluble silver potassium cyanide $AgK(CN)_2$, but the least excess of silver nitrate reacts with this to produce insoluble silver cyanide.—$AgK(CN)_2 + AgNO_3 = 2AgCN + KNO_3$. Similarly, in the titration of a hot solution of sodium phosphate by ammonium molybdate in presence of ammonium nitrate and gelatin, a cloudiness marks the end-point.

D. An alteration in the color or tint of the titrate is noted. If to a solution of a copper salt is added hydrobromic acid there results a deep violet color, and on titrating the mixture by stannous chloride the color persists to the end, then suddenly bleaches. In the titration by iodine of antipyrine in alcoholic solution or of diazo-compounds in ethereal solution, a faint yellow or red tint indicates the end-point. The purple of potassium permanganate is visible even in a highly dilute solution or one slightly tinted by other compounds, and since the decomposition products of this reagent by a reducer are colorless, the titrate remains uncolored up to the end-point, after which the least excess of permanganate is shown by a faint purple tint.

A passive tinctorial body, that may be added to the titrate or one of the products of the volumetric reaction, may be held in solution by the aid of the compound. to be titrated, but being insoluble in one of the products of the volumetric reaction, will wholly precipitate at the close, leaving the liquid colorless or but slightly tinted. Rarely a change in the color of the precipitate itself shows the end-point.

Conversely, there may be compounded with the titrate an immiscible liquid or a solid in fine powder capable of withdrawing and permanently retaining either (a), the chromogen of the colored titrate, or (b), a colored product of a secondary reaction initiated only after the completion of the volumetric reaction; the color of the immiscible liquid is visible when the layers have separated. For example, in the titration of sodium chromate by sulfuric acid to sodium bichromate ($2Na_2CrO_4 + H_2SO_4 = Na_2Cr_2O_7 + Na_2SO_4 + H_2O$); into the titrate is stirred ether containing hydrogen peroxide. When all the sodium chromate has become bichromate the least excess of sulfuric acid sets free chromic acid ($Na_2Cr_2O_7$ +

* Journ. Anal. Chem. 4—427.

$H_2SO_4 + H_2O = Na_2SO_4 + 2H_2CrO_4$), which passes at once into the ether and reacts with the hydrogen peroxide to produce a soluble blue-colored compound plainly visible when the ether is allowed to form a layer above the water.

Another example is that of phosphorus suspended in alcohol, titrated by a solution of bromine in carbon disulfide, phosphorus pentabromide being formed. Any excess of bromine passes into the alcoholic liquid and colors it yellow.

E. By an indicator.* Previous to the titration an adjective soluble in the titrate is mixed with it. The adjective reacts with both titrand and titrate and hence a permanent compound is formed with the titrand only after the volumetric reaction is ended. This secondary reaction produces some visible effect, usually a change in color, less often a turbidity, opalescence or opacity.

For example, the titrate a solution of potassium hydrate, the titrand hydrochloric acid, and the indicator the sodium compound of a certain weak organic radical. On running in a quantity of the hydrochloric acid there is formed an indeterminate mixture of potassium chloride, sodium chloride and free organic acid, but the latter immediately combines with the remaining potassium hydrate to form the potassium compound of the organic radical. At the end of the titration when all the potassium hydrate has become potassium chloride, the least excess of hydrochloric acid reacts with the organic salt and permanently sets free an equivalent of organic acid. At this point occurs a marked change in color of the titrate, since an aqueous solution of the sodium compound of the organic radical is colorless or nearly so, while that of the free organic radical is intensely colored.

For the indicator is selected where possible a compound that will yield a product of a high color by reaction with the titrand. Sometimes the product is colloidal or insoluble but so diffused through the liquid as to color it deeply and uniformly. For example, in titrating a solution of sulfurous acid by solution of iodine, the adjective being soluble starch; as soon as the volumetric reaction is ended ($H_2SO_3 + I_2 + H_2O = H_2SO_4 + 2HI$), the intensely blue iodide of starch is formed with the least excess of iodine. Similarly in the titration of ammonium molybdate by lead acetate, the reaction producing insoluble lead molybdate; the adjective tannin yields a yellow to red color.

F. Among other indications that are of use in special cases may be mentioned the disappearance of a pungent or characteristic odor, and the cessation or incipience of foam on stirring the titrate. It is said that taste† is a highly delicate test in alkalimetric titrations; in titrating picric acid by solution of berberine, both intensely bitter compounds, the end-point is observed by the absence of a bitter taste in a little of the clear liquid filtered off from the precipitate of berberine picrate.

The potential difference of two electrodes immersed in halves of one solution separated by a porous diaphragm, rises from zero as the solute in one-half is precipitated by the titrate, and at the end of precipitation shows a sudden abnormal increase. The potential difference is registered by a delicate galvanometer.‡

Spot indications. When the titrate or a product of the volumetric reaction is dark in color, the change in tint of an indicator cannot be perceived with certainty, if at all. Again there are times when for some reason an indicator cannot be incorporated with the titrate, even near the close of titration. In such cases a 'spot test' takes the place of the usual modes of noting the end-point. A drop of the titrate is withdrawn from time to time during the titration and tested by mixing with a drop of the indicator or another reagent, or in some other way whereby

* Lunge, Chemisch-technische Untersuchungsmethoden, 1—55.

† Chem. News, 1898—1—91.

‡ Chem. News, 1896—2—270.

the color of the titrate does not obscure the exhibition. The test is repeated with each addition of the titrand until the volumetric reaction is complete. The presence of a precipitate or other solid suspended in the titrate has less effect on the distinctness of a spot reaction than the same indication in the titrate.

An example is the familiar method of the titration of ferrous chloride by potassium bichromate, in accordance with the reaction—

$$6FeCl_2 + K_2Cr_2O_7 + 14HCl = 8Fe_2Cl_6 + Cr_2Cl_6 + 2KCl + 7H_2O,$$

the ferrous chloride being oxidized to ferric. The pronounced dark yellow and green colors of the ferric and chromic chlorides mask the yellow tint given by an excess of the bichromate, so recourse is had to a spot indication. A solution of potassium ferricyanide gives no precipitate with a ferric salt but an intense blue precipitate with a ferrous salt. After running a small volume of the bichromate solution into the titrate, a drop of the latter is taken out with a glass rod and mixed on a porcelain plate with a drop of a weak solution of ferricyanide. An intense blue precipitate is observed. After repeating the above several times it is noticed that the precipitate has become much less voluminous, this serving as a warning to run in the titrand in smaller volumes—finally the mixed drops show even no blue coloration, evidencing the entire conversion of the iron to ferricum, or more exactly, that the remaining trace of ferrosum is too minute to visibly react with ferricyanide.

Another example is the determination of chlorine in presence of a salt of copper by titration with silver nitrate. Instead of waiting until the precipitate has settled, as in the usual method, it has been advised to take out a drop of the turbid liquid and let it fall on a polished copper plate. Any excess of silver nitrate produces on the plate a gray film of silver—$2AgNO_3 + Cu = Cu(NO_3)_2 + Ag$. The insoluble chloride of silver does not react with the copper.*

In acidimetry and alkalimetry, a deep-colored liquid can be titrated by spotting on a test-paper—filter paper that has been impregnated with a solution of litmus, lacmoid, turmeric, phenol-phthalein or other medium, and dried; a paper coated with ultramarine is discolored by acids even in highly dilute solutions. Waldblott proposes that a little of the titrate be taken out by a narrow glass tube and the end of the tube pressed against the test-paper; the capillarity of the paper has the effect of conducting away the water from the dissolved matter thus concentrating the latter at the center of the stain and intensifying the indication.

When a colored liquid containing a precipitate is dropped on thick filter paper, the precipitate remains at the spot, while the liquid extends and its color shows plainly around the precipitate and on the back of the paper. A drop of the titrand or other reagent let fall near the margin of the moist circle creeps in contact with it and the color-reaction is apparent before the precipitate is reached.

Indicators. For titrations where the reaction is that of the neutralization of acids by alkalies and earths or their carbonates, or the reverse, an indicator is mixed with the titrate. The color of the solution of an indicator changes instantaneously when the reaction of the liquid containing it turns from acid to alkaline or the reverse.

A great number of artificial and natural organic dyes have been proposed as indicators, and of them the following, with perhaps a few others, have come into common use. They are made up and kept for use in aqueous or alcoholic solution, rarely in other menstrua.

* Journ. Anal. Chem. 2—202.

	One part dissolved in	With acids	With alkalies
Phenol-phthalein	100 alcohol	Colorless	Intense red
Litmus	Infusion	Red	Blue
Methyl orange	1000 water	Pink	Yellow
Cochineal	Tincture	Yellow-red	Violet
Coralline	750 alcohol	Straw	Violet-red
Lacmoid	500 dil. alcohol	Red	Blue
Phenacetolin	500 alcohol	Gold-yellow	Dark pink
Turmeric	Tincture	Yellow	Red
Brazil wood	Infusion	Yellow	Purple-red
Haematoxylin	100 alcohol	Yellow	Orange

The colors may be modified considerably from those stated above by impurities in the indicator and extraneous matters in the titrate, the proportion of indicator to the titrate, and the color of the light.

Indicators are either free acids or bases or their compounds, all comparatively weak, though of different strengths. The change in color at a reversal of reaction is accredited to an alteration in molecular complexity — thus phenol-phthalein is colorless when in the molecular state,* but red when dissociated into ions; the molecule of methyl orange red, the ions yellow, etc. It was remarked by Allen that the indicator must always be weaker in chemical affinity than the acid or alkali to be titrated, and as all the indicators in common use are weaker than the mineral acids and the fixed alkalies, any one is applicable for their reciprocal titration; but many indicators are not as strong as the weaker acids and bases.

Thompson divides indicators into three groups. The first comprises methyl orange, cochineal, Congo-red, lacmoid, indeosin, and dimethylamidobenzene; these react with strong acids only, but are sensitive to bases of feeble affinities such as many alkaloids. In the second group are rosolic acid and phenacetolin, reacting with weaker acids than the first group. In the third are phenol-phthalein and turmeric, sensitive to the weakest acids and indifferent to a great many of the vegetable alkaloids.

Lescoeur defines neutrality as a state wherein on the one hand helianthine remains yellow, and on the other, phenol-phthalein remains colorless and litmus red. An aqueous extract of cocoa-nibs is said to be alkaline to methyl orange and acid to phenol-phthalein, the amphichroism indicating a soluble salt of a weak organic acid accompanied by a small proportion of a free organic acid.

Litmus is weaker than carbonic acid and therefore cannot be used when the acid is present in the free or half-bound (page *v.* Water) state, while the stronger cochineal is unaffected. The alkaloids are bases of so indifferent a character that the acid radical of quinine sulfate, for example, may be titrated by an alkali and phenol phthalein as though it were combined with hydrogen.

The difference in the strength of indicators is at times an advantage, permitting the successive titration of two of the constituents of a substance without their separation. An example is the titration by a caustic alkali of a mixture of a mineral acid with one of the higher fatty acids, based on the indifference of methyl orange to the latter. After titrating with this indicator until the red has changed to light yellow, showing that all the mineral acid has been neutralized, phenol-phthalein is added, and the titration continued for the fatty acid.

Again, in a mixture of sodium hydrate and sodium carbonate (*e. g.* the commercial caustic alkali), the proportions of each can be determined by titration by a standard acid, first with phenol-phthalein, the solution remaining red until all the sodium hydrate and *one-half* of the sodium carbonate are neutralized (sodium bicarbonate is neutral to this indicator)

$$NaCH + HCl = NaCl + H_2O, \text{ and } Na_2OO_3 + HCl = NaHOO_3 + NaCl.$$

* Journ. Amer. Chem. Socy. 1902—591.

this requiring M cubic centimeters of the acid. The sodium bicarbonate remaining is now titrated with the acid and methyl orange,

$$NaHCO_3 + HCl = NaCl + H_2CO_3.$$

requiring N Ccs. The "total alkalinity" is expressed by $M + N$, and the "causticity" by $M - N$ Ccs. of the acid.

The color of an indicator is modified to a greater or less extent when a titration is done by artificial light (except electric). With litmus the transition is obscured by gaslight, though with a sodium (monochromatic) flame the sharpness of the end-reaction is increased, the red appearing colorless, and the blue, black.

When the titrate is colored by organic matter or other bodies, the end-point is more easily seen through a flat glass cell containing a liquid of the same hue. Lupp, as an aid in discerning the end-point by change in color or formation of a precipitate, rests the beaker containing the titrate on a hollow tripod, beneath which is a concave mirror reflecting the sun's rays up through the titrate. The device is also of service in cloudy weather from the increased illumination. Some titrations, however, as of acetone by a hypochlorite, must be performed in subdued light only.

Should one of the soluble products of a volumetric reaction deepen the color of the titrate, possibly it may be withdrawn from solution by some immiscible organic solvent stirred up with the titrate, *e. g.*, iodine absorbed into carbon disulfide.* But in some determinations the accuracy is prejudiced by the contact of organic liquids with the titrate or titrand, and many indicators show abnormal colors under these circumstances.†

The amount of indicator to be used in the titrate should be limited to that actually required, since an excess may lessen the accuracy of a delicate titration, for in many cases *all* the indicator present must react with the titrand before a positive change in color ensues.

Of the great number of indicators that have been proposed, probably litmus, phenol-phthalein, methyl orange and cochineal are most in use. Litmus, the pioneer, is still favored by some chemists over those of more recent introduction, notwithstanding the rather laborious process of preparing the solution of the principle *azolitmine* free from other coloring matters of the lichen.‡ It may be used in hot or cold solutions for the mineral, thiosulfuric, and nitrous acids, the alkalies and earths, and fairly well for the common organic acids except citric. As it is sensitive to carbonic and hydrosulfuric acids, these must be entirely removed from the titrate; easiest by boiling before the titration is begun, if they exist in the free state, or after each addition of the titrand if they are combined with a base.

Phenol-phthalein ‖ is admirable for the fixed alkalies and mineral and organic acids, but, like litmus, it is sensitive to carbonic acid. For free ammonia or in titrating in presence of ammonium salts, a large proportion of the indicator must be in the titrate.§ It may also be used in alcoholic and ethereal solutions.

Methyl orange or helianthin is less delicate than the above even when used for concentrated solutions, and as the pink color is but faint at best, close attention is needed to catch the change; moreover it cannot be used for organic acids nor in hot solutions, yet in spite of these and other drawbacks, it is of great value from its indifference to carbonic and other weak acids.

Cochineal is but slightly affected by carbonic acid, but cannot be used for organic acids or in presence of iron or aluminum salts. Lacmoid is very sensitive and may be used in a strong alcoholic solution where methyl orange is indistinct.

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* Zeits. anal. 1896—305.

† Journ. Phys. Chem. 1898—171.

‡ Chem. News, 1889—2—306 and 1894—2—225.

‖ Journ. Anal. Appl. Chem. 1893—201.

§ Chem. News, 1899—1—214.

Other indicators have special characteristics and are chosen in preference to the foregoing for some special determinations where these peculiarities are of advantage. But for general work, an indicator as delicate and brilliant as phenol-phthalein, and at the same time unaffected by carbonic and hydrosulfuric acids, is yet unknown.

Whenever the titre of a standard acid or alkali or similar compound is stated the indicator used in the standardization should be named.

A 'standard' or 'set' solution is one in which the weight of reagent in the unit of volume (in the metric system, grams in one cubic centimeter) or the chemical change that a unit of volume will effect, is exactly known. It may be stated as (*a*), the weight of reagent in the unit of volume; or (*b*), the active constituent of the reagent in the unit of volume; or (*c*), the weight of a certain body with which the unit of volume reacts.

Thus, a cubic centimeter of "chameleon" solution may be said to contain *a* grams of potassium permanganate or *b* grams of available oxygen, or to be equivalent to *c* grams of oxalic acid. It is immaterial which is chosen, as one may be calculated from another, except in empirical processes where the reaction is more or less vague, incomplete, or modified by the experimental variants of temperature, dilution, etc., and one result comparable with another only when all the conditions are alike—here only the third form of expression is admissible.

The concentration of a standard solution may vary, usually between wide limits. Exceptions are where the solubility of the reagent or its volatility in aqueous solution limits the strength; where the volumetric reaction takes place normally only in a very concentrated or dilute solution, with a reversed or some secondary reaction at a different concentration; or where the indicator is such that a prompt or decisive change is shown only at certain concentrations. But there is never any advantage in making a standard solution weaker than when one drop will distinctly bring out the end point of a titration.

The solvent is usually water, or for reagents insoluble or but sparingly soluble, an aqueous solution of some compound that will not interfere with the volumetric reactions. For some reagents alcohol more or less diluted with water is necessary; bromine and iodine and some organic compounds are dissolved in chloroform, ether, benzol, or carbon tetrachloride, the titrate being a solution in the same liquid; but on account of the volatility of these solvents, great care must be taken to prevent evaporation during titration, and standardizing be done just before a titration.

A few solutions are best made up by dissolving two or more bodies that mutually react to set free the active constituent; this plan is adopted in cases where it is difficult to purify or weigh the reagent. For example, six atoms of bromine are set free on dissolving five molecules of potassium bromide and one molecule of potassium bromate in dilute hydrochloric acid. Frequently the reaction is so definite and complete that the standardization of the solution can be omitted.

Standardizing. Having decided as to the quantity of solution to be prepared, the calculated weight of reagent is to be dissolved in water and made up to the proper volume. For ammonia and the mineral acids and some other liquids the original specific gravity affords a ready means of preparing the volumetric solutions by simple dilution, and the gravity of the solution is a rough measure of the concentration. Tables of concentrations corresponding to the various

gravities will be found in most works on analysis, but an allowance must be made for the contraction in volume on dilution.

The exact titre (concentration) of the solution is now to be established. Several methods are available.*

A. A small measured (or weighed) volume of the solution is evaporated to dryness in a tared dish and the residue weighed. This process assumes that both the reagent and solvent are perfectly pure and that the reagent is not oxidized or otherwise decomposed or volatile at the temperature of boiling water.

If the reagent is an acid, a measured volume may be supersaturated by ammonia and evaporated to dryness at a low temperature. A pure ammonium salt is left and the proportion of acid can be calculated from its weight. Or the acid may be poured on a weighed amount of a fixed metallic oxide or carbonate in fine powder that readily combines with the acid. The liquid is evaporated, dried and weighed, and from the increase in weight, due to the combined acid radical, is calculated the titre. Thus, lead protoxide with sulfuric acid.

B. The reagent or some constituent thereof is precipitated from a measured volume of the solution and the precipitate weighed; as hydrochloric acid precipitated by silver nitrate, the silver chloride weighed, and the corresponding acid calculated. Here enter all the errors of precipitation, filtration, ignition and weighing, and the process is necessarily slow, so that it is less used than the following.

C. The most common method is that of ascertaining what volume is required to neutralize or otherwise react with a weighed quantity of some solid with which it combines. For this purpose we select a substance of a definite chemical composition and prepare a quantity with such precautions as to be positive of its purity, dissolve a suitable weight in water or other solvent, and titrate the solution directly.

The presumption would be, from the abundance of chemical compounds easy to prepare in a pure crystallized or anhydrous form, that no difficulty should be experienced in finding one, if not several, suited to any given volumetric solution, thus providing a ready and exact means of standardization. Yet for quite a number of solutions even one compound, satisfactory in all respects, is wanting.

Crystalline double salts, whose bases are respectively the active and an indifferent principle, have the advantage over simple salts of bearing a higher molecular weight, thus counteracting to some extent the errors of weighing, etc. But, on the other hand, the composition of a double salt is apt to be uncertain, the ratio of the bases varying according to the conditions of crystallization.

Some elements or compounds that are volatile, readily oxidizable, or otherwise unsuited for direct weighing, may be liberated *in situ* from suitable compounds by certain reagents; *e. g.*, iodine is liberated from potassium iodide in aqueous solution by potassium permanganate (the solid or in solution) according to the equation —

$$10KI + K_2O.2MnO.O_5 + 14H_2SO_4 = 5I_2 + 2MnSO_4 + 12KHSO_4 + 8H_2O.$$

One method of standardizing is by stirring into a measured volume of the solution a weighed amount (an excess) of some compound in fine powder that is insoluble in water but reacts to soluble products with the reagent of the solution, then determining what proportion of the powder remains undissolved, and by difference what has reacted. For example, barium carbonate used to determine the strength of hydrochloric acid. The process is subject to at least two forms of error; one, that the point where the acid becomes by neutralization so dilute that it has no action on the base, is indefinite, varying with

* Jour. Amer. Chem. Socy. 1901—727.

the temperature, frequency of stirring, concentration, and the physical condition of the solid; the other, that the solution of a neutral salt may have a greater solvent power for the powder than has pure water. We may therefore have in solution free acid or free base with the neutral salt. Since the two errors have an opposite effect on the result they are to some extent mutually corrective.

For the titration of a constituent of a complex substance where the volume of titrand is increased or diminished somewhat by the influence of associated bodies, the solution is standardized on a synthetic proof as near to the mixture in composition as possible, or on another similar mixture wherein the reacting constituent has previously been determined gravimetrically.

D. A few special methods not included in the foregoing. For example, the standardizing of an aqueous solution of hydrogen peroxide by liberating and measuring the (doubled) volume of the available oxygen of the peroxide — in the reaction with potassium permanganate in an acid solution, an atom of oxygen from the peroxide unites with an atom from the permanganate to form a molecule —

$$5H_2O.O + K_2O.2MnO.O_5 + 3H_2SO_4 = 5O_2 + 8H_2O + K_2SO_4 + 2MnSO_4.$$

one molecule of potassium permanganate reacting with five molecules of hydrogen peroxide.

Of two mutually reacting solutions, if one be standardized, the strength of the other may be found from their volumetric relation and the combining weights of their reagents.

Normal solutions. A normal solution is a standard solution made up of such a strength that in a unit of volume (one liter) is dissolved a weight of reagent equivalent in chemism to a unit of weight (one gram) of hydrogen; for example,

1. Cl (atomic weight 35.45) + H = HCl (molecular weight 36.458); a normal solution of chlorine contains 35.45 gramsof Cl; and one of hydrochloric acid, 36.458 grams of HCl per liter.

2. $AgNO_3$ (molec. weight 169.96) + HCl = AgCl + HNO_3.
normal silver nitrate contains 169.96 grams $AgNO_3$ per liter.

3. KCNS (molec. weight 97.22) + $AgNO_3$ = AgCNS + KNO_3.
normal potassium sulfocyanide contains 97.22 grams KCNS per liter.

4. $HC_2H_3O_2$ (60.032) + KOH = $KC_2H_3O_2 + H_2O$.
H_2SO_4 (98.086) + 2KOH = $K_2SO_4 + 2H_2O$.
H_3PO_4 (98.044) + 3KOH = $K_3PO_4 + 3H_2O$.
normal acetic, sulfuric and phosphoric acids contain respectively 60.032, *one-half* of 98.086, and *one-third* of 98.044 grams per liter.

5. $K_2O.Cr_2O_3.O_3$ (294.42) + 6H (nascent) = 2KOH + $Cr_2O_3 + 2H_2O$.
normal potassium bichromate contains *one-sixth* of 294.42 grams of $K_2Cr_2O_7$ per liter.

As indicated in the above, in a reaction between any two normal solutions exactly equal volumes of each take part. The molecular weights are often the combining ones and equal the number of grams to be dissolved in a liter of water, but there are numerous exceptions.

From the dissimilar nature of the reactions, two solutions that each react volume for volume with a third solution may not agree with each other. If sulfurous acid and potassium bichromate be made normal toward potassium hydrate they will not mutually react in equal volumes; for although

$$H_2SO_3 + 2KOH = K_2SO_3 + 2H_2O.$$

and $K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O$.

yet $K_2Cr_2O_7 + 3H_2SO_3 + H_2SO_4 = Cr_2(SO_4)_3 + K_2SO_4 + 4H_2O$.

With some writers, particularly those of Great Britain, the term 'normal' has not the significance generally adopted, but is held to represent the solution of a molecular weight of a bivalent reagent in the unit of volume.

When an exactly normal solution is to be made, the calculated weight (or as near it as practicable), is dissolved in water and the solution made up to the corresponding volume; the concentration is then ascertained by a suitable method. From this datum it is easy to compute (page 180) how much of either the reagent is to be added to bring up the solution to normal, or of water to reduce it thereto, but from several causes, this process often fails to yield an exactly normal titre, and the testing and adjusting may have to be repeated one or more times before success is attained.

Strictly normal and subnormal solutions of the mineral acids can be prepared by the electrolysis of a metallic sulfate giving free sulfuric acid; for hydrochloric and nitric acids the corresponding barium salts are decomposed by the sulfuric acid.*

But considering the liability of solutions to gain or lose in strength by variations in temperature, evaporation or decomposition, a simpler and much less laborious plan is to forego attempts to prepare and maintain the solutions of a strictly normal concentration, and make them up only approximately normal, correcting for the variations in calculating the results of the titrations.

Sub-normal and super-normal solutions. Instead of the various devices for delivering and reading fractions of a cubic centimeter smaller than tenths, the same accuracy can be attained by the use of solutions weaker than normal — dilution with an equal volume of water giving semi-normal; with nine parts, decinormal, etc. By reason of the volatile nature of some compounds and the limited solubility of some salts, it is practicable to make up their solutions only semi-normal or weaker. As to the question of what strength it is best to make up a standard solution — whether normal, decinormal or centinormal — it is to be considered that although the errors in measuring the volumes and other factors are less in proportion as the solution is more dilute, yet the volume needed to show the end-point distinctly is greater. In general, the concentration of the titrand should be adjusted to the weight of the body to be titrated or vice versa as circumstances admit.

Solutions stronger than normal are used when it is an object to keep the total volume of the titrate small, or when the reaction or end-point indication proceeds best in a highly concentrated solution. It is seldom that one stronger than binormal will be needed.

A list of volumetric solutions commonly used in inorganic analysis follows. The weights are grams of the reagent per liter.

Hydrochloric acid	Normal	36.456
Nitric acid	"	63.048
Sulfuric acid	"	49.043
Oxalic acid, anhydrous	"	45.008
Oxalic acid, crystallized	"	63.024
Potassium hydroxide, anhydrous	"	56.116
Sodium hydrate, anhydrous	"	40.058
Barium hydrate, anhydrous	Decinormal	8.572
Ammonia (NH_3)	"	1.706
Sodium carbonate, anhydrous	Normal	53.050
Potassium carbonate, anhydrous	"	69.110
Arsenious oxide	Decinormal	4.950
Iodine	"	12.685
Sodium thiosulfate, cryst.	"	24.832
Potassium bichromate	"	4.908

* Journ. Amer. Chem. Socy. 1901—12 and 848.

Potassium permanganate	Decinormal	3.162
Iron (as ferrous salt)	"	5.602
Ferrous sulfate, crystallized	"	27.820
Ferrous ammonium sulfate, cryst.	"	39.240
Stannous chloride, anhydrous	"	9.498
Tin (as stannous chloride)	"	5.953
Silver (as silver nitrate)	"	10.792
Silver nitrate	"	16.996
Sodium chloride	"	5.850
Potassium sulfocyanide	"	9.722

Empirical Solutions. In routine technical work where a number of samples of a given raw material or product are periodically tested, the usual calculations are dispensed with by so adjusting the standard solution that one cubic centimeter corresponds to one per cent, one-half per cent, one-tenth per cent, etc., of the reacting constituent of the substance analyzed, of which a certain fixed weight is taken for the titration. A "decimal solution" is one of which ten cubic centimeters reacts with one gram of a given solid or one cubic centimeter of a given liquid.

The concentration of an empirical solution designed for a special material should be such that the smallest volume that can be easily read on the burette used is approximately equivalent to say one-fifth of the probable error of the determination, and the total volume used for a titration of any sample not abnormal in composition be within the capacity of the burette.

Common reagents for titration. For alkalimetry, *sulfuric acid* is easily obtained in the market almost perfectly pure, and can be diluted to a perfectly stable solution. Precipitates are formed with hydrates of the barium group and certain lead compounds, yet the end-point can nevertheless be seen with sufficient distinctness. *Hydrochloric acid* forms soluble chlorides with nearly all the bases and its titre is readily found by means of silver nitrate, but a serious objection is its volatility and although it has repeatedly been claimed that a weak solution can be heated and even boiled without loss by volatilization, yet a conservative operator will generally adopt the certainly non-volatile sulfuric. Of the other acids *nitric* offers no advantages except possibly where secondary reactions might take place with the above; *oxalic* and *tartaric* and their acid salts are not easily procured of so definite a composition as to be weighed directly, they form insoluble compounds with many bases, and are liable to decompose when in solution; *chromic acid* (potassium bichromate) has been proposed, but its deep yellow color obscures the tint of the indicator, especially in a strong solution.

Many schemes for standardizing the acids have been brought forward, though none are entirely satisfactory as combining accuracy and convenience. Potassium and sodium hydrates are not admissible as they always contain more or less water and carbonates, and are extremely hygroscopic. Sodium carbonate, however, can readily be prepared pure and anhydrous, and not being hygroscopic can be accurately weighed. The carbonic acid liberated during the neutralization must be expelled by boiling after the end-point is shown, unless an indicator can be used that is not affected by it. The alkaline reaction is restored by the removal of the carbon dioxide, and alternate additions of acid and ebullition are necessary until no change in color is produced by the latter. A less tedious way is to supersaturate at once with an observed volume of acid, and after boiling determine the excess of acid with standard alkali. Richmond calls attention to the error that may arise from the absorption of carbon dioxide by standard acids, the acidity increased proportionately.

Other methods, more or less used, are the precipitation of sulfuric acid by barium chloride, the precipitated barium sulphate weighed and the concentration

of the acid calculated, this process assuming that the solution contains no sulfate of a base; similarly, hydrochloric acid is precipitated by silver nitrate, oxalic acid by calcium chloride, etc. A solution of pure sodium hydrate can be prepared by weighing a freshly-cut lump of sodium under gasoline, afterward dissolving in alcohol of 90 per cent, and diluting with water. The base of a metallic compound with a weak acid radical, such as boracic, can be titrated directly by a standard mineral acid, with a suitable indicator. Sodium oxalate, a salt that can be prepared pure by repeated crystallization, leaves on ignition pure sodium carbonate that may be titrated directly. Sulfuric acid diluted with hydrogen peroxide solution reacts with standard potassium permangate in a definite ratio (page 125). And it has been advised to make up normal sulfuric acid by dilution of a weighed quantity of concentrated acid with strict attention to temperature.*

Of the corresponding bases, *potassium* and *sodium hydrates* are most in use, though against them may be charged the difficulty of obtaining them free from carbonic acid and protecting their solutions from its absorption, and the corrosion of the glass of bottles used for their storage. The solutions may be purified by the introduction of barium hydrate, avoiding an excess, and Millon's base has been advocated for the purpose, itself practically insoluble. But if practicable, it is the better plan to arrange the titration so that the carbonic acid shall not interfere.

Potassium tetroxalate, sodium biborate, and other acid salts and certain crystallized acids are used for standardization by titration to the normal salts; thus, $KHC_4H_4O_6$ (potassium hydrotartrate) $+ KOH = K_2C_4H_4O_6$ (potassium tartrate) $+ H_2O$, but only after a tedious purification and testing has insured a product of exactly the assumed formula unmixed with either the normal salt or the free acid. Titration of the sulfuric acid liberated by the electrolysis of a weighed amount of pure cupric sulfate in aqueous solution is perhaps the most accurate method that has been proposed.

However, the usual method for standardization is by titration of a standard acid and calculating from their combining weights.

Pure *ammonia* is easy to purchase, acts but slightly on glass, and unlike the fixed alkalies, does not introduce a fixed base into the titrate, which is sometimes an advantage. Like hydrochloric acid, however, its volatility is a serious drawback for general use. *Lime water* and *calcium saccharate* are highly recommended for the titration of free carbonic acid and such organic acids as are found in wine-must: *strontia water* has some advantages over lime water, as in the titration of free acid in fermented milk. *Baryta water* is better suited for the titration of alkaloidal compounds than the caustic alkalies, and any carbon dioxide absorbed from the air immediately combines with barium and precipitates, leaving the liquid perfectly caustic. Potassium bichromate may be used for standardizing, with phenol-phthalein as indicator.

Sodium carbonate can be obtained quite pure and weighed without difficulty. Carbon dioxide is liberated on titrating an acid, and the titrate must be intermittently boiled or a strong indicator employed. It has been proposed to determine the end-point by adding a little barium chloride to the titrate and note the instant when a persistent cloudiness ($BaCO_3$) appears. In presence of certain organic matters a troublesome frothing ensues, but can be dissipated by a thin layer of paraffin or paraffin oil on the titrate.

Alkali solutions of various bases, as *zinc oxide in potassium hydrate*, *copper oxide in ammonia*, etc., have the advantage of being available for dark colored clear liquids, since the end-point is shown by a turbidity due to the separation

* Chem. News, 1895—2—5.

of the base of the titrand. They are not applicable for acids forming insoluble compounds with the base of the titrand nor in presence of their metallic salts.

2. Titration by *iodine* (held in aqueous solution by potassium iodide) may be applied for the determination of a number of bodies, either directly, as for hydrogen sulfide, sulfurous acid, etc., which react with the decomposition of water, or by the intervention of an iodide as in the case of chlorine ($Cl_2 + 2KI = 2KCl + I_2$).

Arsenious acid reacts with iodine becoming oxidized to arsenic acid. The solution is made by combining the but slightly soluble acid with sodium carbonate. *Sodium thiosulfate* with iodine forms sodium tetrathionate ($2Na_2S_2O_3 + 2I = Na_2S_4O_6 + 2NaI$). The end-point of these titrations is shown by the bleaching of the yellow color of the iodine solution (iodine in potassium iodide) or more decisively by the incipience or disappearance of the blue color of iodide of starch when starch paste has been previously introduced in the solution.

3. *Potassium bichromate* ($K_2O.Cr_2O_3.O_3$) easily parts with three, and *potassium permanganate* ($K_2O.2MnO.O_5$) with five atoms of oxygen to reducing agents. The former is in common use in acid solution for the titration of ferrous salts and a few organic bodies, while the latter is more sensitive and decomposes many organic bodies. Ferrous salts are commonly used for standardization, sometimes a hot solution of oxalic acid for permanganate. Bichromate may be used for titrates containing free hydrochloric acid, but with permanganate a secondary reaction occurs interfering with the titration.*

Of all volumetric solutions, that of *potassium permanganate* perhaps approaches nearer the ideal solution than any other. It has a wide application, oxidizing most of the lower inorganic and many organic compounds, is fairly stable and not decomposed by light, air or carbon dioxide, is easily made up and standardized, and from its intense color needs no extrinsic indicator.

The purple tint that marks the end-point fades rapidly, due principally to the spontaneous decomposition of the free permanganic acid to water, manganic oxide and oxygen. The decomposition is hastened by the presence in the titrate of a manganous salt or organic matter.

Permanganate is used chiefly for the titration of acidified aqueous solutions; the most suitable acid is sulfuric, though dilute nitric is equally good for some compounds. It is asserted that *potassium manganate* has some advantage over permanganate as an oxidizer.†

Potassium (or *sodium*) *bichromate* dissolves to a stable yellow solution well adapted for the titration of strong reducers, though from the deep green color of the chromium salts formed in its reduction, a spot indication in necessary. Bichromate is also a medium for the titration of barium and lead compounds, their chromates falling.

Stannous chloride is sometimes used for the titration of ferric chloride, reducing it to ferrous chloride; the indicator is a sulfocyanide, the red ferric sulfocyanide being reduced to the corresponding colorless compound. The solution is readily oxidized by the air and must be restandardized before each set of titrations.

4. Silver and chlorine unite to form the highly insoluble silver chloride. For the titration of solutions containing silver salts is used standard *sodium chloride*, and for chlorides, standard *silver nitrate*. The end-point is the cessation of precipitation, easy to be seen as the precipitate quickly clots, more readily

* Amer. Chem. Journ. 1899—461.

† Chem. News, 1899—1—301.

when silver is in excess. In a neutral titrate of a chloride there may be contained potassium chromate as an indicator, any excess of silver precipitating red silver chromate.

A *sulfocyanide* precipitates silver as sulfocyanide; the indicator is a ferric salt, developing the familiar intense red coloration of ferric sulfocyanide with the least excess of the titrand.

Residual titration—also known as 'reverse titration' or 'titrating back'. This modification is practiced in titrations where the end-point is not easy to discern or the titration tedious or difficult for other reasons. To the titrate is added of the titrand a measured volume in quantity more than sufficient to complete the reaction; the excess is then determined by titration by another volumetric solution reacting with the first and whose volumetric relation to it has been ascertained. It is premised, of course, that the products of the first reaction are indifferent to the second solution. For the first solution it is often more convenient to substitute a weighed amount of the solid reagent that forms its basis.

For example, formaldehyd reacts with ammonia to produce (neutral) hexamethylenetetramine—$6CHOH + 4NH_4OH = (CH_2)_6N_4 + 10H_2O$—but instead of titrating the formaldehyd directly by a standard solution of ammonia, it is more satisfactory to add an excess of standard ammonia at once, then determine the excess by titration with standard hydrochloric acid and a suitable indicator.*

The principle of reversed titration has several applications that are the bases of technical methods, as the following.

Of a mixture of solids, the proportion that is soluble in a reagent can be found by treating the mixture with an excess of a solution of the reagent of known concentration, then titrating back with a solution that reacts with the solvent but not with the dissolved matter. The end-point is observed by an indicator or the turbidity coming from the precipitation of one of the dissolved constituents.

An element or compound to be determined is precipitated from solution by a measured volume of one volumetric solution; after filtering or decanting, an aliquot part of the filtrate is titrated back by a second volumetric solution. A modification useful in some cases is to dispense with filtration by removing the excess of the first volumetric solution by boiling or other means; the suspended precipitate is dissolved in an excess of the second solution, and the excess titrated back by the first.

The determination of the saponification value as applied to an oil or fat is described under Oils and Fats; the process is also resorted to for various other compounds.

In a direct titration when the end-point is inadvertently overstepped, a small measured volume of the second solution may be introduced and the titration resumed more cautiously, not forgetting to deduct in the calculation for a volume of the titrand equivalent to that of the second solution added.

An elaboration of the principle of residual titration is shown in the following examples. The direct titration of sulfuric acid or a soluble sulfate by barium chloride is open to the objection that the precipitated barium sulfate is finely divided and slow to settle, so that the end-point cannot be observed by noting when the formation ceases; and filtering a little of the turbid fluid after each addition of the titrand and testing the filtrate is at best tedious. Indirect methods avoid the filtration and testing, though at the expense of simplicity; a few only are trustworthy. That of Edmunds † requires four standard solutions, and is as follows.

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* Chem. News, 1893—2—2, and Journ. Anal. Chem. 3—459.

† Chem. News, 1896—2—194 and 246.

1. The neutral solution of a sulfate is precipitated by a measured volume (an excess) of standard barium nitrate;

$$Na_2SO_4 + Ba(NO_3)_2 = BaSO_4 + 2NaNO_3$$

2. What remains of the barium nitrate is precipitated by a measured volume (an excess) of standard potassium chromate;

$$Ba(NO_3)_2 + K_2CrO_4 = BaCrO_4 + 2KNO_3.$$

3. What remains of the potassium chromate is precipitated by a measured volume (an excess) of standard silver nitrate;

$$K_2CrO_4 + 2AgNO_3 = Ag_2CrO_4 + 2KNO_3.$$

4. The precipitate, a mixture of barium sulfate, barium chromate and silver chromate, is filtered off and in the filtrate the excess of silver nitrate is determined by titration with standard sodium chloride;

$$AgNO_3 + NaCl = AgCl + NaNO_3.$$

Another method for the same determination is due to Stolle. The principles are these:

(1) When barium chromate is dissolved in hydrochloric acid, there are formed barium chloride and chromic acid both passing into solution —

$$BaCrO_4 + 2HCl = CrO_3 + BaCl_2 + H_2O.$$

(2). If an excess of ammonia be added to this solution the reverse reaction takes place and all the chromic acid falls as barium chromate —

$$CrO_3 + BaCl_2 + 2HN_4OH = BaCrO_4 + 2NH_4Cl + H_2O.$$

But if previous to (2), all the barium is removed by precipitation as barium sulfate —

$$CrO_3 + BaCl_2 + H_2SO_4 = CrO_3 + BaSO_4 + 2HCl —$$

then all the chromic acid combines with ammonia on afterward supersaturing the solution with ammonia, and remains in solution —

$$CrO_3 + BaSO_4 + 2HCl + 4NH_4OH = (NH_4)_2CrO_4 + BaSO_4 + 2NH_4Cl + 3H_2O.$$

and if less than the total barium be precipitated by sulfuric acid a proportionally less amount than the total chromic acid will remain in solution, the remainder falling as barium chromate.

Of a freshly* made solution of a known weight of barium chromate in a certain volume of dilute hydrochloric acid, an excess is added to the sulfuric solution to be assayed. After stirring, an excess of ammonium hydrate is run in, and the precipitated barium sulfate and barium chromate filtered. The filtrate is acidified, and the chromic acid titrated by reducing to chromic oxide by a standard reducing solution, then the excess of the latter titrated back by an oxidizer like permanganate or bichromate.

The basis of a few methods is the titration by a volumetric solution that acts as a solvent of solid matter suspended in water or in some solution; even titrations wherein the solid is transformed to another insoluble compound have been proposed. The success of a titration of this nature depends on several conditions, such as the volume and temperature of the titrate, the rapidity of the reaction, and the subdivision of the suspended matter — thus, a freshly formed voluminous precipitate will dissolve much more promptly than after standing for a time or becoming crystalline or compacted. But as a rule better results are obtained and more quickly by a reverse titration.

The titration of a liquid in which is suspended a precipitate or other solid matter that also reacts with titrand is not uncommon, it being assumed that the reaction will take place preferentially with the solution and the end-point show momentarily before the reaction with the solid begins. Of this class are methods where the base of a neutral metallic salt is precipitated by an excess of standard alkali, and, without filtering, the excess titrated by standard acid; since in a cold dilute solution the indicator turns before any of the precipitate is acted on by the acid. Occasionally the nature of the titrand and of the bodies suspended and in solution is such that should any of the solid be acted on by the titrand, the product of the reaction will itself at once react with the uncombined soluble matter as if it were the titrand; here the presence of the suspended matter may be ignored, although the customary indication of

* Chem. News. 1892—2—168.

the end-point may be so transitory as to require a special provision for the purpose. In all other cases the success of a titration of this kind depends mainly on a high degree of insolubility of the suspended matter and its resistance to combination with the titrand. It need hardly be mentioned that the titrand should be run in slowly — even by drops — and that the liquid be not too concentrated.

In a few instances the compound to be titrated is a comparatively insoluble gaseous radical that must be liberated from the compound during titration by acidification of the solution, *e. g.*, a nitrite titrated by potassium permanganate, liberating the nitrous acid and oxidizing it by alternate additions of sulfuric acid and permanganate to the cold dilute solution.

A few titrations are made fractionally, changing the reaction of the titrate, raising the temperature, or otherwise altering the conditions before the end-point is reached. In these cases two or more reactions are involved, each proceeding only under certain suitable conditions. Only the final product may cause the exhibition of the end-point, or the end of the first reaction may also be manifest.

An example* is a method for the titration of cuprous sulfocyanide by potassium permanganate. By the action of permanganate the cuprous compound is broken up to cupric sulfate and hydrocyanic acid according to the equation —

$$10CuCNS + 7K_2Mn_2O_8 + 21H_2SO_4 = 10CuSO_4 + 10HCN + 7K_2SO_4 + 14MnSO_4 + 16H_2O \quad (1).$$

In the first installment of the titration the cuprous sulfocyanide is decomposed by sodium hydrate, then the cuprous hydrate oxidized to cupric hydrate by titration, a slight excess of permanganate being run in to complete oxidation. In the second installment the titrate is acidified by sulfuric acid, and the sulfocyanic acid oxidized to hydrocyanic acid by titration. The weight of the original cuprous sulfocyanide is calculated from the above equation.

Several reactions are involved in the process. On treating the cuprous sulfocyanide with sodium hydrate it is decomposed to cuprous hydrate and sodium sulfocyanide —

$$CuCNS + NaOH = CuOH + NaCNS \quad (2).$$

On titrating this solution by permanganate there are produced cupric and manganic hydrates —

$$8CuOH + K_2Mn_2O_8 + 8H_2O = 8Cu(OH)_2 + Mn_2O_3.3H_2O + 2KOH \quad (3).$$

The slight excess of permanganate added acts on the sodium sulfocyanide —

$$NaCNS + 4K_2Mn_2O_8 + 10NaOH = 4K_2MnO_4 + 4Na_2MnO_4 + NaCNO + Na_2SO_4 + 5H_2O \quad (4).$$

On acidifying by sulfuric acid, the manganic hydrate in equation (3) and the potassium and sodium manganates and the sodium cyanate in equation (4) react with the sodium sulfocyanide of (2) to form hydrocyanic acid —

$$6Mn_2O_3.3H_2O + 2NaCNS + 11H_2SO_4 = 12MnSO_4 + 2HCN + 28H_2O + Na_2SO_4 \quad (5).$$

$$3K_2MnO_4 + 3Na_2MnO_4 + 4NaCNS + 10H_2SO_4 + 4H_2O = 3K_2SO_4 + 5Na_2SO_4 + 6MnSO_4 + 4HCN + 12H_2O \quad (6).$$

$$3NaCNO + NaCNS + H_2SO_4 + H_2O = 4HCN + 2Na_2SO_4 \quad (7).$$

And on titrating by permanganate —

$$5HCNS + 3K_2Mn_2O_8 + 4H_2SO_4 = 3K_2SO_4 + 6MnSO_4 + 5HCN + 4H_2O \quad (8).$$

That the process as conducted answers to the equation (1) is proved by the net consumption of oxygen from permanganate for equations (3) and (8) being 35 atoms to 10 molecules of cuprous sulfocyanide; and the net consumption in equation (4) agreeing with that in equation (8).

In theory it is immaterial as regards the ratio of their combining volumes, which of two inter-reacting solutions is made the titrand, but in practice there will be found a slight, sometimes a marked, difference due to the excess of the titrand needed to show the end-point, or for other reasons. It is sometimes the better plan to dissolve a material to be assayed in water, make up the solution to a definite volume, and with it titrate a measured volume of a reacting solution than to proceed in the usual way; here the standardizing follows the same routine as the titration.

* Journ. Amer. Chem. Socy. 1900—685 and 1902—580.

For example, picric acid forms an insoluble picrate ($C_{25}H_{31}N_3.C_6H_2(NO_2)_3.OH$) with crystal violet (an alinin dye, the hydrochloride of hexamethyl-rosanilin). For the determination of picric acid in a commercial sample, one gram of the sample is dissolved in a liter of water and added from a burette to a measured volume of a solution of crystal violet until the supernatant liquid assumes a faint yellow tint announcing an excess of picric acid. An equal volume of the violet solution is then standardized by titrating it by a solution containing a known weight of chemically pure picric acid.

A complex substance containing two analogous elements or compounds in the free state or each combined with the same or with different radicals, may often be volumetrically determined without separation.

1. By means of one volumetric solution. One of the bodies may react precedently to the other and the intermission allow a transient exhibition of the end-point, or the incipiency of one of the products of the reaction with the second member be utilized to show the dividing line.* Thus, sulfindigotic acid is completely oxidized by a permanganate before sulfindirubic acid is acted on; lactic acid is neutralized by an alkali before lactic anhydride is saponified.

In a few cases also, the inequality in strength of two indicators may be applied. For the determination of the free acid and the base in an acid solution of a metallic salt, it has been proposed that the indicator be a mixture of phenol-phthalein and methyl orange.† At the beginning the solution is pink from the methyl orange, phenol-phthalein being colorless in an acid solution. On titrating by an alkali the solution turns to yellow at the point where the free acid is neutralized, and the titrate remains yellow until all the base is precipitated, when the least excess of alkali develops the red of the phenol-phthalein, its intensity overpowering the faint yellow of the methyl orange.

The members of some mixtures may be titrated successively under different conditions, one member reacting in the cold, the other only at the boiling point; one reacts in an acid, the other only in a neutral or alkaline solution; etc.

A mixture of two bodies A and B, that react simultaneously but in dissimilar ratios may be determined in one titration. If x represents the percentage of A in the mixture; y, that of B; and 100 of the two; a, the volume of titrand reacting with one gram of A, and b and d the corresponding volumes for B, and the mixture; then $x = 100\frac{d-b}{a-b}$ and $y = 100 - x$.

In technical work are found certain materials that contain two or more analogous constituents possessing an equal or nearly equal value for some practical purpose, and can be determined together by one titration. If there be no reason to the contrary, the result can be reported as the joint content of the constituents, or as the leading member if one greatly preponderates, or the result calculated to units of value for the use intended.

2. The mixture may be successively titrated by two different volumetric solutions. Between the titrations some alteration is made in the titrate, such as changing the reaction from acid to alkaline, filtering off an insoluble product of the first operation, boiling off a volatile product, oxidation, etc. Thus, a solution of two inorganic salts containing free acid; first the free acid is neutralized by standard alkali, then one base changed in valence by a standard oxidizing or reducing solution, and finally the other base precipitated by a suitable standard precipitant. However, it is more usual to effect a partial or complete separation before proceeding with the volumetric determinations.

One element or compound existing in a solution in two different combinations may be successively titrated by two solutions each reacting with only one

* Allen, Coml. Org. Anal. 3—1—123.
† Zeits. anal. 1883—397.

form of combination. An example is a mixture of sodium chloride and sodium hypochlorite titrated by silver nitrate and arsenious acid.*

3. The titrate may be divided and one element or compound determined in each half by different solutions; for example, in one-half a constituent is oxidized or reduced, and in the other half another constituent is precipitated.

Preservation. Volumetric solutions should be stored in a cool dark place in tightly stoppered bottles of chemical glass. The absorption of carbonic and other acids from the air by solutions of the caustic alkalies can be prevented by withdrawing the liquid through a syphon, admitting air to the bottle through a guard-tube containing soda-lime or solid caustic potash. A thin layer of paraffin oil or kerosene floating on the solution will tend to prevent contact of air, though the protective power against oxidation has been overestimated. Where the reagent is an easily fermentable or putrescible organic body, a trace of a preservative, as a mercuric salt, phenol, or salicylic acid, can usually be introduced without its interfering with titrations. The fungoid growth sometimes observed in fifth-normal sulfuric acid is prevented by the addition of a few drops of chloroform.

Too much reliance must not be placed on the unalterability of any volumetric solution. With many of these the efficiency of the reagent lies in the facility and rapidity with which it is decomposed by other bodies, and the solution is correspondingly prone to spontaneous decomposition or sensitive to light, heat, dust, etc. Stannous chloride in hydrochloric acid, hydrogen peroxide in water, bromine in carbon disulfide, and the like, change perceptibly from day to day. Other reagents are more stable and can be preserved for a considerable time without alteration. Yet, all things considered, it is always advisable to verify every solution before each set of determinations. This precaution also eliminates a possible source of error due to difference in temperature at the times of standardization and analysis.

A volumetric solution compounded of two others, one containing the essential principle of the reaction, the other an adjective, may become less active on standing, though apparently the composition remains unchanged. The solutions are best kept separate up to the time of use, then a sufficient quantity mixed in the proper proportions. And where a solution is made up in considerable quantity for regular use, it is well to divide it among several small sealed bottles opened only as required, or to preserve it in a large stock bottle kept sealed and in a dark cool closet, transferring to a smaller one as needed.

Titration. After filling the burette and drawing off the solution to the zero mark, the tap is opened and the solution run into the titrate until the end-point is reached. Allowing a few minutes for the liquid to collect from above the surface, the volume withdrawn is read off. In most titrations, especially when the end is shown by a decided change in color, one can follow the progress of the reaction closely enough to slacken the stream when near the close and finish by delivering a drop at a time, not forgetting to stir continuously throughout.

The most suitable vessel to contain the titrate is a casserole or a wide beaker set on a porcelain plate, as the white surface allows a slight change in color to be more plainly seen.

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* Chem. News, 1892—2—114.

A flocculent, dark colored precipitate obscures the change in color of an indicator, but if the titrate is held in a porcelain dish or a casserole, a margin of clear liquid in which the color can be plainly seen is exposed by allowing the precipitate to settle for a moment and slightly inclining the dish.

In the titration of a chloride by silver nitrate or the reverse, the precipitate of silver chloride quickly balls together on violent agitation of the titrate, and here a flask with a glass stopper is better. If by long continued shaking the interior of the flask becomes clouded with a film of silver chloride, a portion of the clear liquid is transferred by a pipette to another flask for testing.

In titrating hot solutions sufficient heat may be radiated to expand the contents of the burette, and a shield should be interposed, such as a perforated card fixed above the tap; or the tap may enter a long rubber tube terminated by a glass tip, allowing the beaker containing the titrate to stand some distance aside from the burette, and over a burner if it is desired to maintain a boiling heat.

Should the basis of the colored titrate be a fixed alkali, there may be added an excess of ammonium sulfate and the liquid distilled; ammonia is liberated equivalent in alkalinity to the fixed alkali and passes into the colorless or slightly colored distillate and is titrated therein by standard acid. On the other hand, titrates containing free acid are distilled with ammonium sulfate and a measured quantity of standard potassium hydrate; the ammonia in the distillate is equivalent to that liberated from the volume of potassium hydrate added, *less* the amount neutralized by the acid of the titrate.

But in most cases it is the better plan wherever possible, to remove coloring matter by oxidation, evaporation or precipitation; finely divided suspended matter may be entangled by a voluminous precipitate added to or formed in the liquid, and filtered off. Or the basis of the titrate can oftentimes be precipitated or salted out and filtered off, then dissolved.

In a few titrations, as an acid solution of auric chloride titrated by oxalic acid, the titrate must be protected from oxidation by the air. A convenient receptacle is a three-necked Woolf's bottle, the burette tip passing through a cork in the center neck, and a current of carbon dioxide or coal-gas passed in and out of the other two.

When the end-point is not to be perceived by a visible change in the titrate, and the approximate volume of titrand required is unknown, the titration is likely to be very tedious, and time will be saved by duplication, in the first essay roughly finding the volume to within a few cubic centimeters, and in the second to run in at once as much as the first shows can be done with safety. Or the titrate may be divided into three unequal parts, the largest roughly titrated, the second part added and the titration continued, then the smallest added and the titration concluded.

Gutzow* describes an apparatus wherein the titrate, made up to a definite volume, is put in a bottle through the cork of which passes the stem of a thistle-tube reaching to the bottom of the bottle. By compressing the air in the bottle an aliquot part of the titrate is forced up into the thistle and is there titrated, then allowed to recede into the bottle and mix with the remainder of the titrate. The volume of titrand required for the entire titrate is found approximately by a simple calculation, and the titration concluded in the usual way; or if a closer approximation is desired, the above may be repeated. All methods on this principle assume that it is immaterial whether the titrate receives the titrand or conversely.

When the end-point is observed by the change in color of an indicator and the titrate is turbid originally or from the separation of a slowly subsiding precipitate, the color can be made more evident by preparing for comparison a

* Chem. News, 1888—2—190.

solution identical with the titrate and containing the same proportion of the indicator and of the titrand in quantity just short of the end-point.

A device frequently employed where the change in color at the end-point occurs only after some time or when it passes through a transition tint, is that of preparing a number of test-tubes containing equal volumes of the titrate and running in a progressive series of volumes of the titrand. After standing in the cold or at a boiling heat for the proper time, the color or clearness of one of the tubes in relation to the one adjoining shows it to contain equivalent volumes of the reacting solutions.

For example,* glycerol gives a colorless solution in dilute sulfuric acid, potassium bichromate a yellow, and chromic sulfate a green. On boiling a weak solution of glycerol in dilute sulfuric acid with an equivalent amount or less of bichromate the reaction between the two converts the latter entirely to chromic sulfate and the solution becomes pure green. Any excess of bichromate would give a yellowish tint to the green. A determination of glycerol in weak aqueous solution can be made by placing 5 cc. in each of four test-tubes, acidifying by sulfuric acid, and running in .5 cc., 1.0 cc., 1.5 cc., and 2.0 cc. of standard bichromate. After boiling, two adjacent tubes show the dividing line, one being a pure green, the other a yellowish-green. The latter is made a type for a more exact determination; a second series is made up as before but with volumes of the titrand here running tenths of one cc. below that used in the type, and on boiling, the last tube showing pure green is considered as containing equivalent proportions of glycerol and bichromate.

Confirming the graduation. The accuracy of all volumetric ware should be verified by the user — the flasks, by weighing when empty and dry, then filled with water to the mark; the pipettes, by weighing the amounts of water delivered; and the burettes, by weighing every five or ten cubic centimeters drawn consecutively into a light flask; the variation in volume of water at different temperatures being allowed for by the table given, *q. v.* All articles for measuring can be purchased accompanied by certificates issued by an institution of high repute and responsibility, attesting their accuracy or itemizing the extent of the departure therefrom.

Few burettes have an exactly equal internal area throughout the graduated part, and to learn whether the maker has spaced the divisions with regard to the variations — *i. e.*, how nearly they represent true metric volumes — the weights of water drawn from aliquot parts are compared with the weight of the same volume of water at the temperature of the experiment.† If errors of consequence are found, corrections are applied in practice to every reading affected by them.

Unless the interior of the burette has been thoroughly cleansed, water will not flow out completely but leave drops adhering here and there. An effective abstersive is a strong alcoholic solution of potassium hydrate, afterward rinsing with water, dilute hydrochloric acid and water. If a film of grease resists this treatment, it can be removed by allowing the burette to stand for a time filled with a solution of potassium bichromate in dilute sulfuric acid.

A light flask of a capacity of 50 to 100 cc. is cleaned and dried by warming and aspirating the air from the interior by suction through a glass tube; it is then cooled and weighed.

The burette is fixed vertically in its stand, in front of a window if convenient, and after rinsing, filled from a flask of distilled water that has been standing in the balance room for some hours; most of the water is then run out rapidly to carry away any air-bubbles imprisoned in the tap. After refilling, the water is drawn off until the bottom of the meniscus is just behind the zero mark read with the eye at its level; the outside of the tap is then wiped dry.

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* Analyst, 1898—8.

† Journ. Amer. Chem. Socy., 1898—912.

Ten cubic centimeters of water is drawn into the flask and weighed; then an additional ten cc., and so on up to the capacity of the burette. It can safely be assumed that the area of the interior does not vary to any appreciable extent within a space of ten cc. The temperature of the water is noted, and the weights compared with those for the corresponding temperature in the table.

Example. A 50 cc. burette was tested as directed above, the temperature of the water registering 26° Cent.

Weight of Flask.	Grams.	Weight of water.	True weight at 26°.	Actual volume in ccs.	Error in ccs.
	18.569				
10 cc.	28.527	9.938	9.962	9.976	— .024
20 cc.	38.450	9.923	"	9.961	— .039
30 cc.	48.428	9.978	"	10.016	+ .016
40 cc.	58.418	9.990	"	10.028	+ .028
50 cc.	68.400	9.982	"	10.020	+ .020
Total		49.811	49.810	50.001	+ .001

From the above we see that the first ten cubic centimeters drawn out has actually a volume of only $10 \times 9.938 \div 9.962 = 9.976$ cc.; therefore the true volume of a reading of say

7 cc. is $7 \times .9976 = 6.983$ cc.

13 cc. is $9.976 + 3 \times .9961 = 12.964$ cc.

29 cc. is $9.976 + 9.961 + 9 \times 1.0016 = 28.951$ cc., etc.

In this way a table may be drawn up showing the true value of every cubic centimeter of the burette. For all ordinary work, however, no correction need be made for such small inaccuracies as the above.

A method of testing the relative accuracy of the graduations is due to Carnegie.* The burette is carefully cleaned, and the tap joined by a long rubber tube to a funnel containing water and elevated above the burette. Opening the stopcock, water is allowed to enter and rise to the lowest mark. By means of a long-stemmed funnel about five cubic centimeters of some light organic fluid immiscible with water is run in, and the space it occupies is read. More water is allowed to enter until the organic fluid occupies the space next above; the volume occupied is read, and this process continued throughout the entire graduation.

PIPETTES.

The volume of water delivered by each pipette is weighed in a light tared flask. The pipette is mounted in a burette stand, and the end of a long rubber tube drawn over the top. The tube is closed by a pinchcock, this plan allowing the adjustment of the meniscus to the graduation line to be made more closely than when the pipette is stopped by the finger. Water at the temperature of the room is drawn in and run out until the bottom of the meniscus is aligned with the mark, and the drop hanging to the orifice taken off by a glass rod. The water is then run into a tared flask, and one minute after the flow has ceased the hanging drop is removed by touching it to the inside of the flask. The flask is weighed, the temperature of the water observed, and the volume delivered calculated as for the burette. It is the better plan to correct for any material inaccuracy in the analyses than to attempt to establish a new mark should the original one be wrongly located.

MEASURING FLASKS.

These are weighed, first empty and dry, then filled to the mark with water at the temperature stated on the flask. If a balance of the required capacity is not at hand, they may be calibrated with fair accuracy by filling from a tested pipette. If found inaccurate, a second mark is made by a writing-diamond or a keen triangular file, or a record is made of the true volume contained and a correction applied in practice.

Should the water be at a higher temperature than marked on the flask, a correction is applied to the weighings by the formula

* Chem. News, 1891—2—42.

$V = W - w \frac{1 + .000025\,d}{w'}$, where V is the volume of the flask in liters at $T°$; W, the weight of the flask and water at $t°$, the temperature of weighing; w, the weight of the empty flask; w', the weight of one liter of water at $t°$ by brass weights in air; d, the difference between $T°$ and $t°$; and .000025, the cubic expansion of glass for one degree Cent.

MEASURING JARS.

As a rule, the jars provided with a glass stopper are calibrated to *contain*, and those with a pouring lip to *deliver* the volumes designated, but some makers graduate all jars to contain the specified volumes. If used for any accurate work, therefore, the calibration should be carefully examined by means of a tested pipette of say one-fifth or one-tenth of the capacity of the jar.

CHAPTER 6.

GASOMETRY.

The practice of gasometry or aerometry may be divided into two classes, scientific and technical gas analysis. In the former the highest accuracy is aimed at, while in the latter, strict accuracy is not so much an object as that the results of an analysis be obtained quickly. The difference between the two lies mainly in the apparatus and appurtenances used, those for technical analysis being necessarily more compact and portable.

Under a pressure not exceeding 1500 millimeters of mercury and at a temperature above zero Cent., it may be assumed that the volume of a gas varies directly with the temperature and inversely with the pressure upon it, and that the volume of a mixture of gases equals the sum of the volumes of the constituents.

A. In accurate analyses, two graduated glass tubes are used — the *measuring-tube* in which the sample of gas is gauged and its constituents absorbed, and the *eudiometer*, in which is brought about a combination of hydrogen or hydrocarbons with oxygen. The former is simply a straight tube of thick glass, say 25 cm. long and 20 mm. in diameter, one end sealed and the other provided with a lip for transferring without loss an inclosed gas to another container. The eudiometer differs in being about double the length and having two platinum wires sealed in near the closed end, their inner extremities almost touching, while the outer projections are either bent into loops or cut off close to the glass. On connecting the projections to a source of electricity of high tension a spark leaps across the space between their inner ends, kindling the mixture of gases within, which is either combustible of itself or has been made so by the addition of oxygen.

Both tubes are graduated in millimeters, or in cubic centimeters and tenths, from the closed end as zero. Before putting a tube into use it must be ascertained whether the graduation is correct throughout, and if found inaccurate at any point, the proper correction must be applied to the reading of every gas volume comprehending the defective part. The simplest way by which any variation can be detected is to support the tube vertically and pour in small equal volumes of a liquid and note if the height of the column as read on the scale is each time increased to the same extent. Mercury is the most suitable fluid and is measured into the tube from a cup made of heavy glass tubing. The cup has a flat edge and holds a volume of mercury approximating one-tenth or less of the capacity of the tube. After filling the cup and removing any air bubbles adhering to the glass, the excess of mercury due to the meniscus is expelled by pressing down to the edge a flat glass plate. The cup and plate have each a long handle of twisted wire, that the heat of the hand may not expand the mercury.

The mercury in the cup is poured into the measuring tube, with care to avoid air bubbles. As mercury does not adhere to glass, the surface is convex, and

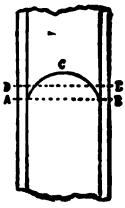

Fig. 112.

the highest point at the center is taken for the reading. Obviously, the empty space surrounding the meniscus, of the form of a plano-concave disk, is included in the reading, and to obtain a true reading it is necessary to flatten the surface which can be done by covering it with a layer of a solution of mercuric chloride, the height being thus lowered to the line D E, Fig. 112. Since the tube is practically of equal bore throughout, all the subsequent readings may be taken at C and the difference between C and D E deducted.

The volume of mercury held by the cup is found by multiplying its weight by .07855 $(1 + .0001814\,t)$, the volume of one gram of mercury at the temperature $t°$ of the experiment. From this datum the capacity corresponding to each space of the tube is calculated, and a table is drawn up showing the true volume of any reading in practice. Where the tube is marked off in millimeters, the capacity per millimeter is found in the same way.

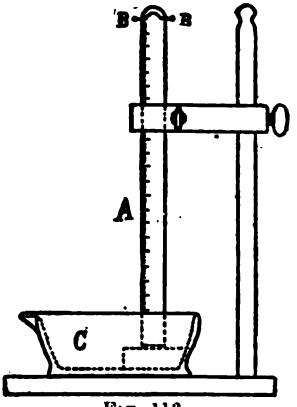

Fig. 113.

Analysis. A drop of water is introduced into the measuring tube, and through a funnel whose stem is long enough to reach to the bottom, it is filled with mercury. The open end is firmly closed by the thumb, and the tube inverted into a mercury trough and held in a vertical or inclined position by the clamp of a heavy retort stand. The trough is made of wood or iron with the front and back of plate glass, or better is made entirely of heavy glass, Fig. 113.

The gas to be analyzed is now passed up, care being taken to avoid loss or introduction of air. If contained in another tube standing over mercury the transfer is made by upward displacement; if in a bulb terminated by narrow sealed tubes, the bulb is held vertically beneath the measuring tube and the ends of the prolongs broken off by nippers; and if in an aspirator bottle, the end of the rubber tube is held under the mercury in the trough and gas forced out until it is judged that all the air has been expelled; then the tube is moved under the measuring tube and the proper volume of gas is allowed to pass up.

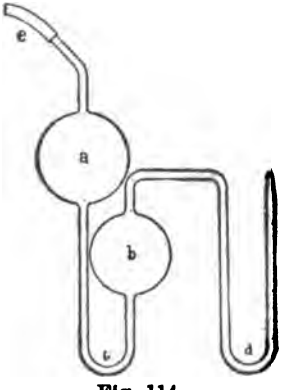

Fig. 114.

A pipette for transferring a gas from a gas tube or gasometer to another tube is shown in Fig. 114. The glass bulbs a and b are of about 50 cc. capacity and connected by the capillary tube c. Over the prolong of a is drawn a rubber tube e. To fill the pipette, b, c, and d are filled with mercury by suction at e, the orifice of d is passed up into the gas of a gas tube standing in a mercury trough, and suction applied to e to draw the mercury from b to a. When b has filled with the gas, sufficient mercury remains in the bend of d to trap it. To discharge the gas, d is immersed in a mercury trough, when mercury displaces the air beyond the bend; then the orifice of d is inserted in the mouth of a gas tube filled with mercury and standing in the same trough, and air blown into e.

In reading the volume of a gas it must be observed that

1. The closed end of the tube, below during the calibration, is now above, so that the error caused by reading the top of the meniscus is doubled and the correction must be doubled accordingly, Fig. 115.

2. The volume of the gas varies directly with the temperature and inversely with the pressure upon it, and the observed volume is to be reduced to the standard temperature (zero Centigrade) and pressure (760 millimeters of mercury).

3. The drop of water introduced in the tube before filling with mercury has saturated the gas with aqueous vapor whose tension or pressure increases that of the gas.

4. The pressure of the external air on the gas is diminished by the difference in vertical height, if any, between the surfaces of the mercury in the measuring tube and the trough.

5. For the most accurate analyses must be taken into account the temperature of the mercury of the barometer (altering its density) and of the barometer scale, the height above sea level, and the capillary attraction between mercury and glass.

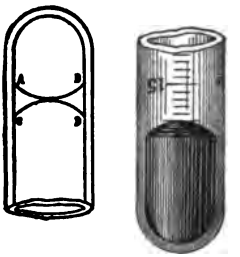

Fig. 115.

The room is left unoccupied for an hour or more that the gas and mercury may come to its temperature. On returning, the operator reads the heights of the mercury in the tube and trough, a thermometer hung beside the tube, and the barometer. These observations are made through a telescope or opera glass from a distance of several feet that the gas may not be expanded by the heat of the body. The normal volume of gas is then calculated by the rules on page 183.

The proximate constituents of the gas are now to be absorbed seriatim by suitable reagents. Those commonly used are

Water. Absorbs bromine, chlorine, ammonia and the gaseous acids; carbon dioxide slowly.

Absolute alcohol. Hydrocarbons of the series C_nH_{2n+1} and C_nH_{2n+2}.

Sodium phosphate. The halogen acids.

Moist potassium hydrate. All acid gases, carbon dioxide, hydrogen sulfide and water.

Dilute sulfuric acid. Ammonia.

Concentrated sulfuric acid. Water, alcohol, ether, methyl oxide, propylene.

Fuming sulfuric acid, or *bromine water*. As in (4) and also methane and its homologues;* and by the acid, benzene.

Phosphorus. Oxygen.

Palladium. Hydrogen.

Reagents used in aqueous solution are

Alkaline pyrogallate or *ferrous tartrate*. Oxygen.

Cuprous chloride in acid or ammoniacal solution. Carbon monoxide, acetylene, oxygen.

Ferrous sulfate. Nitrogen protoxide (N_2O).

Chromic acid or potassium permanganate. Hydrogen sulfide and sulfurous acid.

Palladious chloride. Oxygen.

Potassium hydrate is introduced into the measuring tube in the form of a solid ball on the end of a long platinum wire, made by casting the melted commercial hydroxide in a bullet mold having a groove filed in one of the jaws to

* Journ. Amer. Chem. Socy. 1899—245.

admit the wire. The ball is moistened, immersed in the mercury in the trough, wiped free of air bubbles with the fingers, and passed up in the tube (which is inclined to about 45°) into the gas. It is allowed to remain there for an hour or more; after withdrawing and reading the volume of the remaining gases another ball is passed up to test the completeness of the absorption; if complete the diminution of the original volume is the volume of the gas or gases absorbed by the alkali.

Liquids are introduced by means of a pipette with upturned orifice, and withdrawn by the same instrument or by passing up a tuft of moistened absorbent cotton. Or a porous ball of papier-mache or of carbon (made by igniting a mixture of powdered coke and bituminous coal) may be fixed to the end of a long wire and saturated with the liquid.

Small amounts of certain gases can be more accurately determined by withdrawing them from the mixture into solid or liquid reagents, then dissolving the reagent in some solvent that will retain the gas, and determine it by a gravimetric or volumetric process. Thus, hydrogen sulfide can be absorbed by potassium hydrate, afterward dissolved in very dilute hydrochloric acid and the gas titrated by iodine.

After the absorbable gases and the moisture have been eliminated, there may remain a mixture of hydrogen, various hydrocarbons and nitrogen.* This residue, or a portion of it, is transferred to the eudiometer, and pure oxygen, in excess of what is judged will be needed to form water and carbon dioxide when combined with the hydrogen and carbon of the gases, is introduced. After observing the total volume, the lower end of the eudiometer is clamped down firmly upon a sheet of rubber cemented to the bottom of the trough, or if the eudiometer is provided with a stopcock, it is closed. The exterior projecting ends of the platinum wires are connected with an induction coil excited by a battery. A spark leaps from the inner extremity of one wire to the other, the complete combination of the gases being evidenced by a sharp flash of light throughout the mixture.

To increase the certainty of a complete combustion, a measured volume of oxy-hydrogen gas may be passed up into the tube before the explosion. Pure oxygen and hydrogen, mixed in the exact ratio to recombine to water, are furnished by the decomposition of dilute sulfuric acid by the electric current ($H_2SO_4 + H_2O = H_2 + SO_4H_2 + O$).

Fig. 116.

Bunsen's apparatus for the electrolysis is shown in Fig. 116. At the surfaces of the two platinum plates are given off hydrogen and oxygen respectively, these mixing in the reservoir and displacing the dilute acid. As the solubilities of the gases in the dilute acid vary ununiformly with the temperature, it is important that the temperature of the liquid remains the same during the generation, and this is provided for by surrounding the jar with water. The gas evolved at the beginning of the electrolysis is allowed to escape, the composition being doubtful. Before passing to the eudiometer the gas is dried by passing through a tube containing concentrated sulfuric acid.

To guard against the danger of the eudiometer breaking from too great expansion of the gases at the instant of combination, the pressure on the gas is reduced to below atmospheric by raising the eudiometer so high that there is a considerable difference between the levels of mercury in the tube and the trough. This also lessens the danger

* Journ. Amer. Chem. Socy. 1899—393.

of converting a part of any nitrogen in the mixture to an oxide of nitrogen from a high temperature induced by the explosion.

After the explosion there remains water (in vapor or condensed), carbon dioxide, and nitrogen. The mixture is transferred to a measuring tube and the carbon dioxide determined by absorption by potassium hydrate. If the original gases were perfectly dry, the water formed may be measured by raising the temperature to near 100° and reducing the pressure to one-half an atmosphere, when the water becomes steam.

From the data of the volumes of the combustible gases, the oxygen added, and carbon dioxide and nitrogen, may be calculated the proportions of the hydrogen, hydrocarbons, and nitrogen in the original mixture.*

A number of modifications of the original apparatus, more or less complicated, have been designed to secure greater convenience and safety and shorten and simplify the operations. Full descriptions of these will be found in works on gas analysis and elsewhere.†

Simple devices for evading the calculations of gas volumes from observed conditions to the normal (dry gas at zero and 760 mm. of mercury) have been described by Gibbs and others. In that of Gibbs moist air is inclosed in a measuring tube, measured, and the volume calculated to normal conditions. This "companion tube" hangs in a large trough of mercury, and whenever a volume of gas is to be measured the tube containing it is brought to the side of the companion tube and raised or lowered until the surfaces of mercury in the tubes are at the same height. Since both the air and gas are at the same temperature and under the same pressure, then —

Observed volume of gas : its true volume : : observed volume of air : its true volume.

Keiser's apparatus‡ dispenses entirely with graduated tubes. The principle is, that as the gas to be measured enters a bulb filled with mercury, an equal volume of mercury is forced out and can be collected and weighed and its volume calculated. Omitting some details of construction, it may be described as follows: —

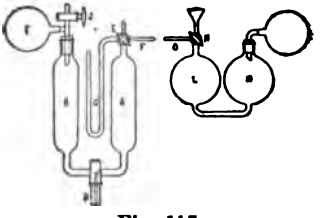

Fig. 117.

In Fig. 117, A and B are two cylindrical glass bulbs, each of 150 cc. capacity, terminated below by tubes uniting in the three-way stopcock C which is so constructed that a passage may be opened between A and B or the contents of B drawn out through the tap D, as desired. The upper end of A is closed by the three-way cock E which may be turned to connect either with F or the U-tube G, both these having a capillary bore. The bulb B is closed by a rubber stopper holding a tube J attached to a rubber bulb K with reversible valves, which on compression and relaxation, either forces air into B or withdraws it, according to the position of the valves.

As an illustration of the manipulation of the apparatus, let it be required to determine the carbon dioxide in a chimney-gas. Mercury is poured into B and by working the pump K, A is completely filled with mercury to E; B is then emptied through C. The tube F, containing a drop of water, is connected with the chimney, and C is turned to open A into B; mercury flows into B until the surfaces are at the same level, drawing in gas from the chimney (about 75 cc.). C is turned to the left, and the mercury in B runs into a tared beaker and is weighed. Dividing the weight by the specific gravity of mercury at the observed temperature gives the volume of gas indrawn; this volume may be reduced to the normal by the usual calculation (page 183). If desired, any greater volume of gas up to the capacity of A may be drawn in by means of the pump K.

The absorption pipette is shown in Fig. 117. It consists of two glass globes L and M

* Sutton, Volumetric Anal. 505.

† Watt's Dict. of Chem. 1—242; Chem. News, 1890—2—196; Journ. Amer. Chem. Socy. 1900—343.

‡ Chem. News, 1887—2—30.

connected at the bottom. At the top of L is a stopcock N connecting it with the capillary tube O. L and M are half filled with the absorbing reagent, here a concentrated solution of potassium hydrate. To transfer the gas from A to L, the reagent is forced up in L to the stopcock N, and the tubes F and O are joined by rubber tubing; by compressing the bulb K the gas is made to pass into L. When the absorption is complete the residual gas is returned to A, its volume ascertained as described above. To be assured that the gas in A is neither above nor below atmospheric pressure, the stopcock E is turned so that A communicates with the manometer tube G; this is half filled with water, and the levels in the arms will be unchanged if the pressure of the gas in the right limb equals that of the atmosphere in the left.

When, as is usual, the temperature and pressure of the atmosphere do not materially change during an analysis, the weights of mercury corresponding to the different constituents of the gas are directly proportional to their volumes, and the calculation is very simple.

The "nitrometer" is an apparatus designed particularly for the generation and measurement of nitrogen or nitrogen dioxide, though often employed with advantage for other gases. One of the many forms is shown in Fig. 118. The burette A is closed at the top with a stopcock B opening in the funnel C. The burette is graduated downward, from the stopcock taken as zero, to 50 Cc. The lower end is contracted and joined by a long rubber tube to an open level-tube D of the same diameter as A.

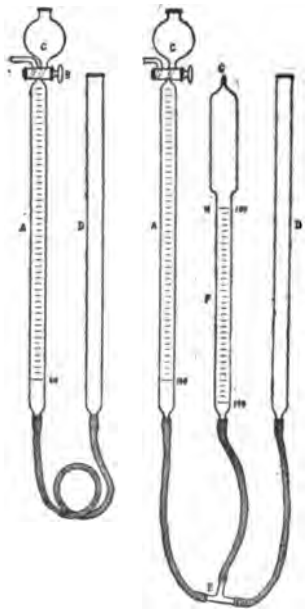

Fig. 118.

The burette is filled with mercury by pouring in at D until A and D are more than half full; then elevating D until the mercury in A rises to the stopcock, and closing B, when the apparatus is in readiness for a determination.

Given a sample of an impure nitre to determine the KNO_3 contained. A solution of a nitrate mixed with mercury and an excess of sulfuric acid reacts to form nitrogen dioxide —

$$2KNO_3 + 5H_2SO_4 + 3Hg = 3HgSO_4 + 2KHSO_4 + N_2O_2 + 4H_2O,$$

one cubic centimeter of nitrogen dioxide measured at zero and 760 mm. being evolved from .004524 gram of KNO_3.

About .2 gram of the sample is weighed, dissolved in a little water, and transferred to the funnel C; D is lowered and the stopcock opened and when the solution is drawn into the burette it is followed by a little rinsing water. Double the volume of concentrated sulfuric acid is then drawn in, cautiously, that no air may enter. The burette is shaken, B being closed, until the reaction is at an end, and after cooling, the tube D is raised to such a height that the pressure on the nitrogen dioxide equals that of the atmosphere. The volume is read, reduced to standard conditions, and the percentage of KNO_3 in the sample calculated from the equation above.

Since an aqueous solution floats on the mercury in A and the reading is taken at its surface, the level of the mercury in D must be somewhat above that in A that the pressure be atmospheric. The difference in height is $\frac{hg}{g'}$, h being the height of the column of aqueous solution, g its specific gravity, and g' the specific gravity of mercury. In technical analyses of a given material where the volumes of the solutions and their specific gravities are practically constant in

all analyses, the tube D may be so graduated as to show the proper level for any volume of gas to be measured.

To save the trouble of calculating the gas volume from the observed temperature and pressure to the standard, in Lunge's "gas-volumeter", * Fig. 118, a 'reduction tube' is introduced. The rubber tube joining A to D has a T-tube inserted at E, the third branch being joined to the reduction tube F; this is calibrated to hold exactly 100 cc. from the orifice G to the mark H, and beyond H graduated down to 140 cc. It is prepared once for all in the following way: The temperature and barometric pressure of the air of the laboratory are noted and the volume saturated with moisture corresponding to 100 cc. of dry air at zero and 760 mm. of mercury is calculated. A drop of water is put into G and mercury poured into D until it has risen to the division on F corresponding to the calculated volume. The orifice G is then sealed with the blowpipe and the apparatus is in readiness for use.

Having the gas to be measured (saturated with water) in A, the heights of D and F are so adjusted that the mercury in F stands at the mark H, and in A at the same level. Then, since both the gas and the air in the reduction tube are saturated with moisture, and at the same temperature and under the same atmospheric pressure, the volume of gas in A as read is the volume of dry gas at zero and 760 mm.

Moore † proposes to determine the weight of certain metals in solution by the weight of oxygen combined in the course of a reaction that converts a proto- to a per-salt, *e. g.*, cobaltous to cobaltic sulfate. —

$$2CoSO_4.(NH_4)_2SO_4 + O + H_2O = Co_2(SO_4)_3.(NH_4)_2SO_4 + 2NH_4OH.$$

the conversion to persulfate takes place only in an alkaline, not in an acid, solution. The weight of the reacting oxygen is determined from its volume, this by the diminution in volume of a measured volume of air.

The apparatus Fig. 119A consists of a tube A graduated in cubic centimeters and decimals upward from zero, and terminated at each extremity by a bulb B and C, each provided with a stopcock, B′ and C′. The acidified solution of cobalt sulfate is run into B and made up to the zero mark with water. The stopcock C′ is closed and strong ammonia water forced into the apparatus through B′ (by connecting the prolong of C′ by a long rubber tube to an elevated aspirator-bottle filled with ammonia water). B′ is closed, and the apparatus shaken vigorously to mix the air of C and A with the liquid. Then the solution in B is replaced by water by admitting water through C′, at the same time running out the solution by B′. Finally the temperature of the remaining air plus nitrogen is brought to that at the beginning of the experiment, the pressure made atmospheric by means of a level-tube, and the height of the liquid read on the scale. The diminution in volume is the oxygen that has taken part in the reaction, one atom corresponding to two atoms of cobalt. The absorption of oxygen due to sulfates of metals other than cobalt associated with it may be neglected provided they have been previously brought to the per-state; an exception is manganous sulfate, whose interference, however, can be minimized by the addition of citric acid.

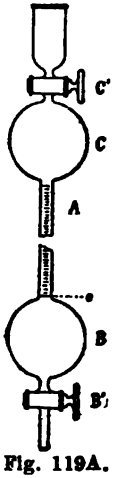

Fig. 119A.

The gas balance of Lux‡ is a glass globe mounted at one end of a balance beam whose opposite end is a pointer traversing a scale. The gas enters at the fulcrum passing by a narrow tube into the globe and out again at the fulcrum. By means of a counterpoise on the pointer-arm the pointer is made to register 100 when the globe is filled with air; the scale is divided into 100 equal parts so spaced that the pointer shall mark 7 when the globe is filled with hydrogen (specific gravity .07, air at 1). The sensibility of the beam can be altered by adjusting screws at the fulcrum.

* Chem. News, 1892—1—45.

† Chem. News, 1892—1—76.

‡ Chem. News, 1888—2—4 and Journ. Franklin Inst. 1898—205.

Lux (loc. cit.) has devised a method for the analysis of a mixture of gases by a series of the gas-balances connected by tubing and having between each adjoining two a bulb holding a reagent to absorb a specific gas. When a mixture is run through the series, from the differences in the readings of the balances may be calculated the proportions of the constituent gases by the formula $X = 100\,\frac{d-b}{a-b}$, where d is the specific gravity of the original gas; a, the gravity of the gas absorbed, and X its percentage in the original mixture; and b, the gravity of the residual mixture.

Siegurt and Duerr manufacture an apparatus on a somewhat similar plan for continuously showing the relative proportions of carbon dioxide and carbon monoxide in a producer gas or a chimney gas. Down to a certain economical minimum, the smaller the proportion of carbon monoxide in a chimney gas, the more perfect the combustion of the fuel; on the other hand the calorific value of a producer gas is in proportion to the content of carbon monoxide, neglecting the hydrogen and hydrocarbons contained. The apparatus is a glass globe sealed up and fixed to one end of a balance beam and counterpoised by a weight at the other end; a pointer traverses a scale and registers the rise and fall of the globe. Through an air tight box inclosing the globe and beam there flows continuously a slow current of the gas. As the ratio by volume of the carbon dioxide (specific gravity 1.5290) to carbon monoxide (specific gravity .9674) increases, the globe is buoyed up in proportion and the pointer rises, and conversely.

The determination of a gas by absorption and weighing, though otherwise unexceptionable, requires a much larger volume than when measured, by reason of the low specific gravity of the gas. The mixed gases are slowly forced through a train of U-tubes and bulb-tubes filled with granular solids and liquids, each tube or bulb absorbing a single gas or the members of a group. The general arrangement of such a train is determined by the nature of the gases to be absorbed and their proportion in the mixture.

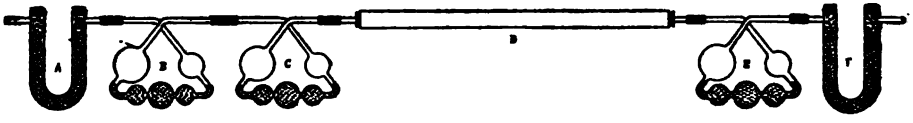

Fig. 119.

One is shown in Fig. 119; the measured quantity of gas enters the U-tube A containing dry calcium chloride to retain aqueous vapor, then passes through B filled with a strong solution of potassium hydrate to absorb carbon dioxide and other acid gases; then to C containing a solution of pyrogallol in potash lye for the absorption of oxygen; then through a porcelain tube D filled with granular copper oxide kept at a red heat by burners below, the hydrogen, carbon monoxide and hydrocarbons being burned to water and carbon dioxide. Beyond D is a calcium chloride tube F and the potash bulb E whose objects are the same as A and B (in the cut F should precede E). The tubes and bulbs are weighed before and after the passage of the gases, the increase representing the weight of gas retained. Guard tubes of calcium chloride may be attached to the absorption bulbs with advantage, for the purpose of retaining any moisture carried off from the absorbents by the gas current.

A process that has many applications is that of liberating a gaseous radical, alone or in combination, by heating, treatment with an acid or alkali, or otherwise. The evolved gas may be measured, but more usually is passed into

some solution with which it reacts. If the absorbent is a measured volume of a volumetric solution, the excess may be titrated back; otherwise the weight of the gas is found by a gravimetric determination.

B. Technical analysis. While the results obtained by the foregoing methods are unexceptionable as regards exactness, the unhandiness of the apparatus and the length of time consumed in an analysis have led Hempel, Winkler, Elliott, and others to devise portable apparatus for technical work by which results accurate enough for the purpose can be quickly obtained. The principal differences are the substitution of water (rarely saturated brine or petroleum) for mercury as a trapping liquid, and the provision of a convenient means for bringing the gases in contact with the absorbents. Of the many types, two will be described — those of Bunte and Orsat.

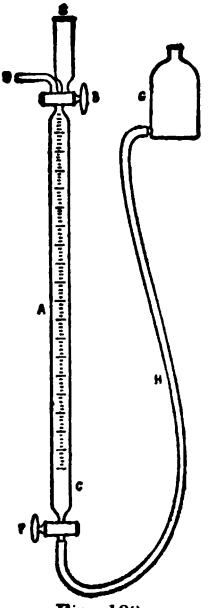

Fig. 120.

Bunte's burette, Fig. 120 holds 100 Cc. from the stopcock B to C, graduated into cubic centimeters and tenths. The stopcock B is a 'three-way' and according to the position of the plug opens a passage from A to E or from A to D or closes all communication. An ordinary stopcock F terminates the burette at the bottom. An aspirator bottle G filled with water is connected to F by a long rubber tube H.

Given a mixture of say carbon monoxide, carbon dioxide, oxygen and hydrogen to be analyzed. The stopcocks F and B are opened and G raised until the burette is filled with water; D is then connected with the gas reservoir and G lowered until somewhat more than 100 Cc. of the gas is drawn into the burette. B is then opened to E, and G raised until the surface of water in the burette stands at zero; F and B are closed. There is now inclosed in the burette exactly 100 Cc. of gas at the temperature and pressure of the air of the laboratory, and saturated with aqueous vapor.

The funnel E is now filled with a strong solution of caustic potash; after removing the rubber tube H from F, a beaker is placed beneath the burette. B is then opened slightly so that a slow stream of the solution may flow down the interior of the burette and absorb the carbon dioxide. When no more will enter, F is opened and the remainder of the potash run through, followed by enough water through B to wash it entirely into the beaker. These operations can be easily performed without any loss of gas or ingress of air. B is closed, the tube H slipped over F, and G raised until the surfaces of water coincide. The volume of the remaining gases is deducted from 100, the difference being the volume of carbon dioxide absorbed.

The oxygen is taken up in the same manner by an alkaline solution of pyrogallin, and the carbon monoxide by an acid solution of cuprous chloride, the nitrogen remaining.

To provide against changes in the temperature of the laboratory during the analysis, the burette is inclosed in a water jacket. This is a large cylindrical

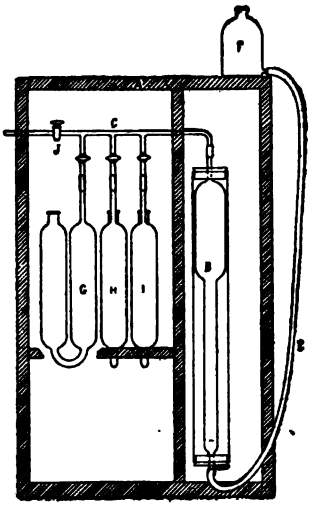

Fig. 121.

glass tube, the ends closed by rubber stoppers through which pass the terminal tubes of the burette. The space between the burette and jacket is nearly filled with water whose change in temperature is so slow that the temperature of the gas in the burette is maintained practically constant during an analysis despite a moderate rise or fall in the temperature of the surrounding air.

The original apparatus of *Orsat* has been modified by Fischer, Muencke, Lunge, Salleron, and others.* All the parts are of glass and are inclosed in a portable wooden case A, Fig. 121, the front and back being removable. The gas burette B is graduated in cubic centimeters from the zero near the bottom, the 100 mark being located just at the stopcock J. A water jacket surrounds the burette. A long rubber tube E joins the bottom of the burette to the tubulus of a water bottle F, and the top is joined to the capillary tube C having three branches each joined to a large U-tube G, H, and I, each containing a solution of a reagent. I is half filled with strong caustic potash solution for the absorption of carbon dioxide, H with an alkaline solution of pyrogallol to retain oxygen; and G (here turned through 90° from its normal position) with a hydrochloric solution of cuprous chloride to absorb carbon monoxide. The outer end of the tube C is connected to the gas reservoir, interposing a tube filled with cotton to retain soot and tarry matter of the gas.

The performance of the analysis is simple and rapid. The burette being completely filled with water, the front limb of each U-tube with its reagent and their stopcocks closed, 100 cc. of the gas is drawn into the burette by lowering F. J is then closed and the bottle raised higher than C. On opening the stopcock of I water rises in the burette and forces the gas into the front limb of I, the reagent receding into the rear limb. After running the gas back and forth a few times to promote its intimate contact with the potash, it is brought entirely into the burette, the stopcock of I closed, the surfaces of water in B and F brought to a level, and the diminution of the gas volume read.

The oxygen is absorbed in a similar way in H, and the carbon monoxide in G. To burn the hydrogen and hydrocarbons remaining, a measured excess of air is drawn in through J, and the mixture run into a receiver and back through a heated capillary tube containing finely divided palladium; this metal has the power to induce the gases to burn in transitu to water and carbon dioxide, marsh gas excepted.

The lower half of the burette is of tubing considerably smaller than the upper half. The reason for the inequality is that the apparatus is designed mainly for producer and flue gases of whose constitution by volume nitrogen forms more than one-half, and as each of the other gases is absorbed, the volume of the remaining gases is read on the graduation of a tube so narrow as to admit of a comparatively accurate observation.†

* Journ. Amer. Chem. Socy. 1899—1106 and 1896—343.

† *Idem*, 1897—859.

A short account of some practical applications of gasometry may be of interest.

1. Determination of carbon in steel and iron. Lunge's improvement* of Wiborg's apparatus is shown in Fig. 122. It is made entirely of glass, for the reason that the chemicals used in the flask might act on cork or rubber fittings and carbon dioxide be generated. The flask A has a funnel-tube t sealed in, and into the mouth is ground the lower end of a condenser d. The upper end of the condenser connects by a capillary tube f to the three-way stopcock h of the Lunge burette B. The burette is fitted with a level-tube D and a reduction tube C.

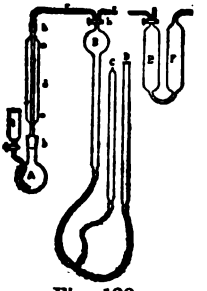

Fig. 122.

For an analysis a weighed amount of steel drillings is placed in A and covered with a saturated neutral solution of cupric sulfate. In the ensuing reaction (page 345), the carbon of the steel separates as a black powder in combination with hydrogen and oxygen. The apparatus is connected as shown and the air removed from A by turning h to connect with A and lowering D. The mercury sinks in B, rarifying the air in A. Then h is turned to open B to i, and D is raised expelling the air from B. These manipulations are repeated until a fairly high vacuum is produced in A, finally leaving B filled with mercury.

Through the funnel t is introduced into A a solution of chromic acid in sulfuric acid; when heated, chromic acid reacts with carbon to form carbon dioxide ($3C + 4CrO_3 = 3CO_2 + 2Cr_2O_3$). D is lowered, h is opened to f, and the solution boiled for an hour. The carbon dioxide with some oxygen and the remaining air is cooled in passing through the condenser, and the excess of water vapor condensed and returned to A. Part of the carbon dioxide remains in the liquid and space in A, and to transfer it to the burette a few cubic centimeters of solution of hydrogen peroxide in water is run in through t, and mixing with the excess of chromic acid reacts with the generation of oxygen ($2CrO_3 + 3H_2O_2 = Cr_2O_3 + 3H_2O + 3O_2$), which displaces the carbon dioxide. Hot water is then drawn in at t (by lowering D) until it reaches h which is then closed.

There is now in B all the carbon dioxide mixed with oxygen and the residual air. D is raised until the mercury in C stands at 100; then D and C raised or lowered until the levels of mercury in B and C are the same. The volume of the mixed gases is then read.

An Orsat's tube E F (page 148) containing caustic alkali solution is attached to i and the mixed gases forced into it; the carbon dioxide is absorbed. The oxygen and nitrogen are brought back into B and their united volume read as before. The difference in the readings is the volume of carbon dioxide under normal conditions, from which the weight of the original carbon may be calculated.

2. An apparatus constructed by Schiebler was formerly in extensive use in sugar refineries for the periodical testing of bone-black for calcium carbonate, its proportion diminishing as the bleaching power of the bone-black weakens by use. The apparatus is arranged for a rapid and fairly accurate estimation on the principle of measuring the volume of carbon dioxide evolved on treating the bone-black with an acid. A modification due to Bernard is shown in Fig. 123.

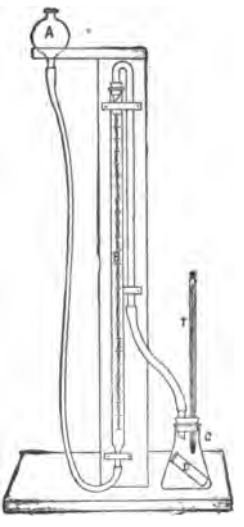

Fig. 123.

The apparatus is in three parts, a flask for the generation of the gas, a burette for measuring it, and a level-tube. The funnel A is supported by a shelf above, and the bottom connected by a long rubber tube to the bottom of the burette B. The burette has a capacity of 100 Cc. and is graduated down from zero near the top in cubic centimeters and tenths. The top is closed by a rubber stopper holding a downward-bent glass tube, this joined by a rubber tube to the flask C. Through the stopper of the flask passes a thermometer T, and inside is a test tube D of such a length that it stands in an inclined position as shown.

Water is poured into A until it has risen to a short distance above the zero mark on the burette. A weighed quantity of the bone-black is placed in C, and the test-tube D is three-quarters filled with dilute hydrochloric acid and carefully lowered to the position shown. The stopper of the flask is pushed in tightly, this compressing the air within to such a degree as to depress the water in the burette a few divisions below the zero mark. A is then lowered until the levels of water coincide, and the burette is read.

* Engineering and Mining Journ. 1891—68.

The flask is tilted so far that the acid runs out of the test-tube and saturates the bone-black; the carbon dioxide evolved depresses the water level in the burette and correspondingly raises it in A. But at the same time A is lowered at a rate that will keep the levels about the same — this to guard against leakage through imperfect connections by a pressure above atmospheric of the air and gas within.

When no more gas is evolved, A is raised or lowered until the levels are the same, and the burette is read. This reading, minus the previous one, is the volume of carbon dioxide evolved at the temperature shown by the thermometer, and from it is calculated the weight of the calcium carbonate. The usual precautions are taken against a rise in temperature of the air and gas. A source of error is the retention of gas dissolved in the acid and is recognized in the tables furnished with the Schiebler apparatus showing the percentage of calcium carbonate corresponding to any volume of gas. The absorption of carbon dioxide that has diffused into the burette and come in contact with the water is practically inconsiderable; in Schiebler's apparatus the air and gas are prevented from mixing by a slack partition of thin sheet rubber.*

3. Reichenberg† has devised a modification of Coquillon's apparatus for the examination of air containing fire-damp. As the apparatus is to be used in mines it is made as compact and portable as possible. In Fig. 124, A is a pipette whose outlet tube is graduated and enters a rubber bulb C filled with mercury. By turning a thumbscrew fixed in the bottom of the jar of water B, the bulb is compressed and mercury forced up to fill the pipette. The top of the pipette is connected with a capillary T-tube, the right-hand limb having a bulb D containing a platinum spiral that may be heated to redness by an electric current, and terminates in the gasometer E containing caustic soda solution.

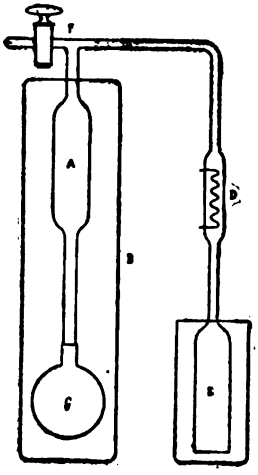

Fig. 124.

The pipette is filled with mercury, and the air to be tested is drawn in through F. The air is forced into E to absorb any carbon dioxide contained, then drawn back into A and measured. The spiral in D is heated to redness and the air drawn back and forth over it to burn the methane to carbon dioxide and water by combination with the oxygen of the air, the former being absorbed by the soda. Finally the residue is drawn into A and measured. The diminution in volume divided by three (one of methane to two of oxygen) is the volume of methane in the air.

4. Clowes‡ has proposed to determine the carbon monoxide in air by drawing it through a box with a glass front in which is a burner fed with hydrogen. The almost invisible flame is regulated to be .4 inch high When the air passing through the box contains .25 per cent of carbon monoxide or other combustible gas the flame-cap (ghost) is increased to .5 inch. A scale is fixed behind the flame, and a pointer runs through the top of the box which may be raised or lowered so that the point at the bottom touches the flame. The box is covered with a focusing cloth, the pointer depressed until the flame is touched, the cloth is removed and the height of the pointer read on the scale.

In solids, gases may be occluded in cavities (blowholes, the pipe) or in pores, and in viscous liquids as bubbles minute and slow to segregate. The identification and determination of these gases is often a matter of scientific and practical interest as denoting the origin of a material or the circumstances of its production or subsequent treatment.

Where the cell-walls are thin and easily ruptured by internal pressure, the inclosed gases can be withdrawn in large measure by strongly heating in vacuo, thereby producing a considerable pressure on the cell-walls and at the same time lessening their tenacity. A practically complete evolution follows

* Crookes' Select Methods, 586 and 594.

† Chem News, 1896—1 -158.

‡ Journ. Chem. Socy. 1896—742.

when the substance can be melted at a moderate heat or at least becomes a semi fluid. An apparatus for the purpose is shown in Fig. 168; the substance is contained in the combustion tube, which is exhausted by the mercury pump, the evolved gases passing to the gas-measuring tube.

An infusible material is reduced to powder, the fineness depending on the size and shape of the gas-containing cavities and their proportion in the solid, as if comparatively large and abundant, a considerable part of the gas would be lost on trituration; on the other hand, if small and scattered, the rupture and penetration of the cell-walls by the inclosed gases is less difficult the more the stability and resisting strength is reduced by subdivision.

Should the solid be soluble in a simple solvent or a solution of some reagent not acting on the gases, they may be liberated by dissolving therein in vacuo and pumped into a gas-measuring tube. A fair proportion of the gas contained in bodies of a fibrous structure and with elongated pores (*e. g.*, charcoal) is expelled when the solid is suspended in water which is then alternately boiled and cooled while maintaining a vacuum.

A molten metal may absorb or occlude many times its volume of gases, liberating them in part before or at the moment of solidification. The phenomenon of 'sprouting' noticed in a large silver button as it chills in a cupel, and the boiling up of a steel ingot in a mold, are examples.

Metallurgists agree that all varieties of iron and steel contain more or less of the gases carbon monoxide, nitrogen, hydrogen, and oxygen, and perhaps carbon dioxide and hydrocarbons, but differ as to their proportion and influence on the physical qualities of the metals. Pig iron is believed to contain the least, wrought iron more, and steel — exposed as it is to the intimate contact of air while in a molten condition, inducing extensive gas-generating molecular reactions, and by reason of the rapid passage from a liquid to a solid — the greatest amount. According to Howe,* nitrogen, hydrogen, and carbon monoxide may exist in iron or steel in three if not four fairly distinct conditions: *A*, non-gaseous or condensed, (1) in chemical combination, exemplified by particles of cuprous oxide diffused through melted copper; (2), in solution, corresponding to the solution of a solid in a liquid; (3), in adhesion, where physical forces predominate, as in the absorption of ammonia in the cells of charcoal; and *B*, gaseous, (4), mechanically retained in the pores or cavities, as bubbles of air in ice. A purely mechanical treatment will set free all the gases in (4), perhaps also in (2) and (3), but not in (1).

It will readily be seen that a determination under such conditions presents many difficulties, and while many methods have been proposed, all are lacking in practicability or certainty. The main reasons are, that weight for weight, the proportion of gas to metal is excessively minute, and that the analytical difficulties, such as the hazard of introducing a trace of air or the products of combustion of the heating arrangement into the complicated apparatus for the determination, are almost insurmountable. That the results on the same material do not agree is further explained by (1), the metal being heterogeneous as regards the gases, from the unequal size and ununiform distribution of the cavities due to conditions of manufacture or coming from cold-working, local expulsion of gas by heating or distortion of the metal, or possibly by osmosis or migration; (2), heterogeneous as regards the impurities of the metal, some (perhaps all) of these influencing the metal to retain the gas, or by inter-reactions of the gases with the metal or its impurities on heating or distortion of the metal during or after manufacture.

The gases mechanically retained in the pores of the metal may be liberated

* Howe, Metallurgy of Steel 105 et. seq.

by simple comminution. Mueller's apparatus for the purpose is an ordinary dull flat steel drill fixed vertically in a tank of water, oil, or mercury, with the cutting edge upward. Beneath the surface of the liquid and resting on the point of the drill is the lower end of a bar of metal which is slowly rotated by a simple mechanism. As the drill penetrates the bar the metal is ground off, rather than cut, by the dull drill, and the gases are set free and collect in the conical depression, from whence they may be removed from time to time by a gas pipette and transferred to a eudiometer for analysis.

On heating in vacuo a metal in the form of powder or foil, the gases, except those chemically combined, are set free, and may be pumped into a gas measuring-tube. The completeness of the evolution depends on the attenuation of the metal, the degree of vacuity and the temperature.

Hydrogen may be determined by heating the finely divided metal alone or intimately mixed with powdered cupric oxide, in a current of oxygen. The water formed is caught in a tube containing phosphoric anhydride, and weighed. Conversely, oxygen by heating in a current of hydrogen, but here as the metal itself does not enter into chemical combination with the transmitted gas, the evolution is less complete than in the case of heating in oxygen whereby the metal is nearly or entirely converted into oxide. For the current of hydrogen may be substituted nitrogen. It has been proposed to determine the oxygen in commercial copper by melting with tin in an electric furnace in a current of carbon monoxide, weighing the carbon dioxide produced.

Nitrogen can be determined in steel and iron by the Will and Varrentrapp process as used for the nitrogen of an organic body. The metallic powder is mixed with soda-lime and heated in a combustion tube and the ammonia formed by combination of the nitrogen with hydrogen collected in a dilute acid and determined.*

A more accurate scheme is to dissolve the steel in hydrochloric acid, the nitrogen combining with the nascent hydrogen evolved. The solution, now containing ammonium chloride, is gradually added to a boiling solution of sodium hydrate, the alkali being in excess of what is required for neutralization of the free acid and precipitation of the iron as ferrous hydrate. The alkali is contained in a closed flask connected to a bulb-tube containing water or a dilute acid into which the liberated ammonia distills.

In either case the ammonia is determined by Nessler's solution (page—). The result includes any ammonia present as such in the steel — several observers have reported the escape of ammonia gas from fresh fractures of cold steel.

Carbon monoxide burns to carbon dioxide when the metal is ignited in a current of oxygen. After drying the gases by passing over anhydrous phosphoric acid, the carbon dioxide is caught in a potash bulb and weighed. The result includes any carbon dioxide occluded in the steel.

Carbon dioxide is expelled more or less completely when the finely divided metal is heated in nitrogen or hydrogen; it is caught and weighed in the usual way.

ILLUMINATING GAS.

In ordinary coal-gas are contained various heavy hydrocarbons, mainly ethylene, but also propylene, acetylene, butylene, various members of the paraffin series, etc.; hydrogen and carbon monoxide; also smaller amounts of carbon dioxide, oxygen, nitrogen, hydrogen sulfide, carbon disulfide, and allied bodies.

* Blair, Chem. Anal. of Iron and Steel, 195.

A scheme of analysis* follows, conducted in the ordinary forms of apparatus for gasometry.

1. The *carbon dioxide*, usually very small in amount, is determined by passing the gas through a potash bulb and noting the increase in weight.

2. The *oxygen*, by absorption in a freshly made up solution of pyrogallol in potassium hydrate.

3. *Ethylene* is absorbed by bromine water, limiting the time of contact. The fumes of bromine remaining in the residual gas are removed by sodium hydrate solution.

4. *Benzene* is absorbed by Nordhausen sulfuric acid, afterward removing the fumes by sodium hydrate.

The separation of ethylene and benzene is only approximate, as bromine water slowly absorbs benzene.

5. *Carbon monoxide* is taken up by a freshly made up solution of cuprous chloride in ammonia. The ammonia fumes are removed by dilute sulfuric acid.†

6. *Ethane, propane, butane* and most of the *methane* is absorbed by paraffin oil, which should contain no members volatile below 100°.

7. The residue is mixed in a eudiometer with oxygen and exploded. The carbon dioxide formed comes chiefly from the methane unabsorbed in (6); it is determined by absorption in potassium hydrate.

8. A volume of the original gas is mixed with oxygen and exploded. The carbon dioxide formed is absorbed by potassium hydrate, and the excess of oxygen by alkaline pyrogallol; the residue is *nitrogen*. *Hydrogen* is determined by difference.

9. *Ammonia* is determined by passing a volume of ten cubic feet or more very slowly through a tube filled with glass beads saturated with weak standard sulfuric acid. The excess of acid unneutralized by ammonia is titrated by standard ammonia and haematoxylin.

10. *Hydrogen sulfide*. From 40 to 50 liters of the gas is passed through an ammoniacal solution of lead acetate. The precipitated lead sulfide, mixed with tarry matter, is filtered and oxidized by fuming nitric acid, converting the sulfide to sulfate and destroying the tarry matter. The lead sulfate is determined by the usual gravimetric method.

In the method of Wright, the gas is first passed through dilute sulfuric acid to absorb ammonia, and calcium chloride to dry it, then through a tared tube filled with cupric phosphate which retains the hydrogen sulfide.

11. For *carbon disulfide* and allied bodies have been proposed several methods.

The carefully dried gas is passed through a saturated solution of potassium hydrate in alcohol. The carbon disulfide reacts to form potassium xanthate — $C_2H_5OH + KOH + CS_2 = KC_2H_5COS_2 + H_2O$. The solution is diluted with water and neutralized by acetic acid; the xanthic acid is titrated by standard cupric sulfate which precipitates cuprous xanthate, the end-point shown by potassium ferricyanide. Or the titration may be done by standard iodine — $HC_2H_5COS_2 + I = C_2H_5COS_2 + HI$.

In another method, the gas, mixed with five volumes of pure air, is passed first through lead acetate solution to remove hydrogen sulfide, then over heated platinized asbestos or spongy platinum which burns the carbon disulfide to sulfuric acid; then into a solution of potassium carbonate. The potassium sulfate produced is precipitated by barium chloride as usual.

* Chem. News, 1891—1—15.

† Journ. Amer. Chem. Socy. 1898—343 and 1900—16.

12. Total *sulfur*. The gas is passed through a scrubber containing dilute sulfuric acid to retain ammonia. It then passes to a small burner which is fixed beneath a cone-shaped glass shade. To the burner is supplied pure air for combustion, and a constant supply of ammonia gas is passed over the gas jet. The ammonium sulfate formed by the combustion of the sulfur under these conditions deposits on the sides of the shade and may be dissolved off, precipitated as barium sulfate, and weighed.

Another method directs to burn the gas in pure air and collect the sulfuric acid formed in absorption bottles containing a dilute solution of potassium carbonate. The gas passes through a small gas meter, thence to a micro-burner surrounded by a metal cylinder. Above the cylinder is a glass cone, the two joined by a gutter filled with mercury. The products of combustion pass from the cone to three absorption bottles whose exit tube is connected to a vacuum air pump. Air is supplied to the burner through a pipe leading from a jar filled with pumice saturated with potassium hydrate solution.*

Below is an analysis of South Metropolitan gas made by the above method.

Hydrogen			47.9
Illuminants	Ethylene series, approximate		3.5
	Benzene series, "		.9
	Methane series	by explosion	33.3
		by paraffin oil	7.9
Carbon monoxide			6.0
Carbon dioxide			....
Oxygen			.5
Nitrogen			....
			100.0
Total illuminants (ethylene, benzene, methane)			45.6

* Journ. Amer. Chem. Socy. 1898—702.

CHAPTER 7.

ATTRIBUTIVE METHODS.

In the preceding pages has been described the direct determination of the mass of a body by means of the properties of weight and volume, or the measure of a chemical reaction. We will now consider certain methods based on other properties, common or special, that stand in a definite relation to mass. These properties may be either intrinsic or extrinsic, physical or chemical.

In discussing these methods let us first regard a simple mixture of the body to be determined A with another B. Two cases are presented.

1. Where A has a certain measurable property not exhibited by B or practically inconsiderable, and its value for A is (a), beyond a normal reduction, not modified by admixture with B; or (b), is altered more or less by their juxtaposition or an inter-reaction.

(a) Here only the determinations of a constant of A in the pure state and of the mixture are required. The percentage of A is found from the simple proportion —

The constant of the mixture : the constant of A :: the percentage of A in the mixture : 100 per cent.

For example, a red pigment in fine powder has a color expressed by 42 units. The pigment is made up of a compound whose color value is 78 units and a pure white powder; hence the percentage of the compound in the mixture is 53.8.

(b) In most cases the physical constants of the mixture are not in direct ratios to the proportion of A but are modified by the influence of B on A. Sometimes the influence of B is so small as to be practically negligible, but more often seriously affects the resultant value. The aberration may proceed regularly as the proportion of A in the mixture increases, when the calculation under (a) applies followed by a predetermined correction.

But if proceeding irregularly, or when the correction cannot be expressed by other than an approximate formula the only recourse is to determine the constants corresponding to a progressive series of mixtures, and compare therewith the constant of the mixture in hand. The magnitude of the intervals between successive members of such a table, intermediate numbers being obtained by interpolation, is governed by the aberration from the normal resulting from the presence of B. Obviously, the labor of compiling a table of this kind is only repaid where a large number of determinations are to be made, although for technical work it need only comprise such proportions of A to B as are commonly found in the article examined, the limits being usually far less than a range from none to 100 per cent of each body.

2. Where both A and B possess a common property but to an unequal extent, the two mixing (a) without, or (b) with modification of the composite value of the property.

(a) The equation representing the relation of a constant of two bodies to the resultant constant of their mixture is $aX + bY = 100d$, where $X + Y = 100$ per cent. Hence the formulae

$$X = 100\,\frac{d-b}{a-b} \text{ and } Y = 100\,\frac{d-a}{b-a} = 100 - X.$$

X being the percentage of A in the mixture, and Y that of B; a, the value of a certain constant of A; b, that of B; and d, that of the mixture.

Graphically, if the ordinates are percentages from zero to 100, and abscissæ the constants from a to b, the value of X is read at the intersection of the abscissa of the constant of the mixture with a right line from a to b.

The above formulæ hold good where one of the constants is negative as related to the other. They also apply not only where X and Y are elements or definite compounds, but also where either or both are mixtures of two or more bodies having an identical — or at least an approximately equal — constant.

In applying the above formulæ, it must be observed that the constants are expressed *as related to* a uniform weight of the bodies they represent, and not as a fixed constant to different weights of the bodies. For example, the Koettstorfer Number of an oil is the number of milligrams of potassium hydrate required to saponify one gram of the oil, and here the above formulæ apply: but the saponification equivalent of an oil is the number of grams of oil saponified by one liter of normal alkali, and here for the values of a, b, and d in the equations must be substituted their reciprocals.

The above equations may be combined to the forms —

$$a = \frac{100\,(d-b) + b\,X}{X} = \frac{100d - bY}{100 - Y}$$

$$b = \frac{100d - aX}{100 - X} = \frac{100d - a\,(100 - Y)}{Y}$$

$$d = \frac{aX + b\,(100 - X)}{100} = \frac{a\,(100 - Y) + bY}{100}$$

for the purpose of determining a constant of either body when the constant of the other and the proportions of the constituents are known, or to find the theoretical value of d. The former is of use when one body may be any member of a group which it is desired to identify, the latter in determining experimentally whether the two constituents are miscible without alteration of the resultant constant.

In the technical analysis of a mixture one may be able to easily determine the nature and proportion of one body, while the identity of one or two others cannot readily be made out. But if several constants of the known body and the mixture be ascertained, the corresponding constants of the other may be calculated from the above equations, and by comparison with tables of constants the nature of the unknown body be inferred. And sometimes with two or even three unknown bodies, the figures corresponding to the mean of their constants may at least authorize a conjecture as to their identity.

For example, a lubricating grease, after the elimination of some mineral matter, was separated by saponification into a certain percentage of paraffin and a fatty acid from a fat. The specific gravity, ether value, and heat of sulfuric decomposition was determined for the paraffin and the mixture, and these constants calculated for the saponifiable fat by the above formula. By comparison with a table for the animal and vegetable fats it was found that those for tallow best agreed. Other considerations tended to confirm the deduction.

A physical property exhibited by solutions of some bodies may diminish regularly as the solutions are diluted, while of others the diminution proceeds abnormally, and in a mixture of a body of each class, observations taken at various dilutions may allow a deduction of the proportions of each.

If the two bodies A and B do not make up the whole of a mixture, but there is also Z per cent, determinable directly or by difference, of a third constituent C having a constant-value of zero, the formulæ become

$$X = \frac{100\,(d-b) + bZ}{a-b}, \text{ and } Y = \frac{100\,(d-a) + aZ}{b-a}$$

In some mixtures the constant of one or both constituents may be so great that experimental errors become excessive, and to reduce it to a reasonable figure, both the pure constituent and the mixture are diluted with a known proportion of another body whose corresponding constant is practically nil, or at most is a definite small number. On the other hand, where a mixture has such a composition that the resultant constant is not exhibited to a degree that is easily measured, a weighed quantity of one of the constituents in a pure state is added to the mixture and corrected for in the calculation of the results.

But if, as is more usual, the third constituent has also the property common to the other two, then the values of a second common constant must be determined for each constituent and the mixture, the equations standing —

$$X + Y + Z = 100. \quad X = 100 \frac{(d-b)(c'-b') - (c-b)(d'-b')}{(a-b)(c'-b') - (c-b)(a'-b')}$$

$$a X + b Y + c Z = 100\, d. \quad Y = 100 \frac{(a-c)(d'-c') - (d-c)(a'-c')}{(a-c)(b'-c') - (b-c)(a'-c')}$$

$$a' X + b' Y + c' Z = 100\, d'. \quad Z = 100 \frac{(a-d)(a'-b') - (a-b)(a'-d')}{(a-c)(a'-b') - (a-b)(a'-c')}$$

in which a, b, c, and d are respectively constants of the three constituents X, Y, Z, and their mixture, and a', b', c', and d' are the corresponding values of the other constant.

(b) The resultant value of the physical constant is modified by the admixture of the constituents. If, as in 1 (b), the divergence proceeds symmetrically with the increase of A in the mixture, a correction may be applied by means of an algebraic or logarithmic expression. But in most cases a correction of this kind is applicable only for a limited range of the constitution of the mixture.

For occasional determinations of mixtures of two bodies by this method, an approximate correction for the inter-reaction may be calculated as follows. Having determined d and calculated X and Y by the usual formula (page 155), a synthetic proof, $X' + Y'$, is made up with the same percentages. On the proof is determined d'; should there have been no inter-reaction, then d would equal d'. If there is a difference beyond experimental errors, it is due to the inter-reaction of the constituents. X'' is calculated, using d' in the formula, and the proportion $X'' : X' :: X' : m$ solved, m being the true percentage of X in the mixture. This is on the presumption that the variation of d from the normal is practically the same throughout a small range in the composition of the mixture, and is manifestly less true as the aberration is greater. It is often necessary, and generally advisable to compound a second proof in conformity with the corrected percentages, then repeat the process as above.

Of the various physical characteristics, those of density, color, rotation of polarized light, boiling, melting and congealing points, and refraction of light are in frequent use; there may also be applied viscosity, thermal and electrical conductivity, specific heat, vapor pressure, capillary ascent, voltaic energy, and penetrability.

SPECIFIC GRAVITY.

We may define the mass of a body as the total amount of matter irrespective of external conditions; the density as the volume of the body under specific conditions of temperature, and pressure; the weight as an expression designating the force of gravity upon the body at any given locality; and the specific gravity as the ratio existing between the weight and that of an equal volume of a given standard under like conditions of temperature and pressure.

In determining the specific gravity of a solid or liquid, pure water is made the standard of comparison. Since the density of water and other liquids and solutions varies considerably with the temperature, it is important that the

temperature of the water be stated, as also that of a liquid compared with it. The usual temperatures chosen for the purpose are zero or 15° Cent., sometimes 17.5°, 20°, or 100°.

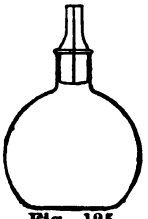

Fig. 125.

In taking the specific gravity of a liquid it is all-important that the volumes be measured with great exactness. The ordinary specific gravity bottle is a light glass flask, Fig. 125; the glass stopper is hollow and ground to fit the flask, the upper part of the bore being a capillary tube. They may be purchased of a capacity of exactly 25, 50, or 100 Cc. at a fixed temperature — usually 15° Cent., or holding approximately one of these volumes, the exact capacity to be determined by the operator.

The size of the flask best suited for a given determination depends on the degree of accuracy required in the result, equal errors in weighing and elsewhere having less effect the greater the volume used in the test. For liquids that differ but slightly in gravity from pure water, one-half or one liter is a suitable volume.

The liquid to be tested is brought to the temperature specified and the bottle filled to the brim; the stopper is inserted and fills, the excess overflowing through the tube. After wiping the exterior, the whole is weighed and the gravity calculated from the difference in weight from pure water at that temperature.

A serious objection to this apparatus is the difficulty of retaining exactly the same temperature during the weighing, a slight increase causing an overflow through expansion. Improved forms have a long narrow tube extending from the stopper marked at a point near the bottom, so that the liquid may expand into it; in some forms the tube is so graduated from zero near the bottom as to show the height to which it is to be filled with a liquid at any given higher temperature to equal the capacity of the flask at the normal temperature.*

Since glass vessels expand on heating, the capacity of the flask or tube will increase with the temperature of the liquid inclosed. Landolt's formula, neglecting a correction for vacuum weights, is $V = \frac{P}{d}$, V being the capacity of the flask; d, the density of water at the temperature t; and P the weight. For any higher temperature t', the volume V' is $V' = \frac{P}{d}\,[1 + .000025\,(t' - t)]$, taking .000025 to be the cubic expansion coefficient of chemical glass for 1° Cent. The employment of temperatures higher than ordinary is a necessity with bodies melting at a moderate heat.

A very convenient and simple apparatus is the Sprengel tube, Fig. 126. A light glass U-tube is terminated by two capillary branches C and D respectively .25 and .50 Mm. in bore, with a mark E around the middle of D; during the weighing the orifices are closed by small glass caps not shown. C is inserted in the liquid, which is then drawn in by suction at D until the tube is filled to beyond E. By touching a strip of filter paper to C the column of liquid in D is made to recede until the meniscus reaches E, the tube C remaining filled by reason of its smaller bore. If inadvertently the liquid is drawn beyond E, a drop of the liquid hanging to a glass rod will be taken in if touched to D.

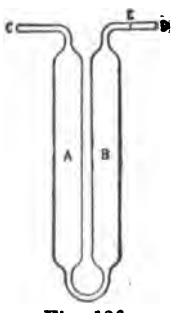

Fig. 126.

For determinations at temperatures above the normal, the tube is filled and hung in a beaker of water or oil so that the body of the

* Ephemeris, 1897.

tube is completely immersed. The bath is heated to the required temperature, and as the liquid expands the excess escapes through D. The meniscus is then brought to E, the tube removed from the bath and cooled, and weighed after closing by the caps.

That a solid immersed in a liquid loses in weight to the extent of the weight of an equal volume of liquid is applied in the Westphal and similar balances. The one shown in Fig. 127 is simply a light horizontal balance beam A supported near one end on a knife-edge. On the left-hand end is a pointer showing that the beam is horizontal by its alignment with a stud B fixed to the supporting frame; and to the opposite end is hung by a fine platinum wire a plummet C whose volume is exactly five or ten Cc. — it is usually a thermometer. The left arm of the beam is made so heavy that the beam will float when the plummet is attached, and also when the plummet is immersed in water at a temperature of 15° and a weight of five or ten grams (in the form of a hook D) is hung on the arm at the division marked 1. The space between the knife-edge and 1 is divided into ten equal parts, and if the plummet be immersed in say an oil of .900 specific gravity, the beam will be poised when the weight is at the division marked .9, etc. Weights of .500, .050 and .005 gram are also provided for determining the gravity to the third decimal. For liquids of greater specific gravity than water, a heavier plummet is provided.

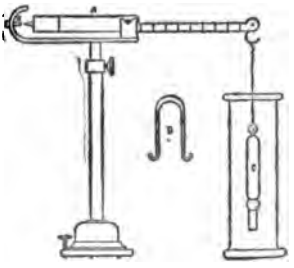

Fig. 127. 1/6

Taylor* proposes as a ready means of determining the gravity of a liquid to weigh therein a plummet whose specific gravity equals its weight in air in grams. The difference between the weight of the plummet in air and in the liquid is the specific gravity of the liquid. If more convenient the weight of the plummet may be a decimal multiple or divisor of its specific gravity, with a corresponding correction of the result.

The hydrometer, Fig. 128, is a light glass tube weighted at the bottom with mercury or shot so that the hydrometer will float in a liquid in a vertical position with the surface of the liquid meeting some point on the upper narrow stem; in some instruments the mercury forms also the bulb of a thermometer inclosed within the tube. Within the stem is a scale, the division which coincides with the surface of the liquid being taken as the reading point. In the instrument for heavy liquids the scale usually ranges from 1.000 near the top to 1.800 near the bottom, and in that for light liquids the 1.000 mark is near the bottom decreasing upwards, usually to .700. A hydrometer graduated to compass so great a variance cannot be divided closer than the hundredths place of decimals and be of convenient length, therefore this range is better distributed among four hydrometers graduated in thousandths, say 1.000 to 1.200, 1.200 to 1.400, etc.

Fig. 128. 1/5

Warrington† claims that an accuracy as great as one part in one million may be obtained by a form of hydrometer that can be wholly immersed in the liquid. Small ring-shaped platinum weights are slipped over the ungraduated neck of a glass hydrometer until the latter has nearly attained the specific gravity of the liquid to be tested. The temperature of the liquid is then slowly altered until the hydrometer and liquid have exactly the same density.

* Chem. News, 1888—1—138.
† Chem. News, 1898—2—144.

Instead of the graduation in units and decimals of specific gravity, certain hydrometers are marked with empirical scales. The most common of these scales are the Beaumé, for liquids lighter or heavier than water, and the Twaddle, for heavy liquids only. They are exclusively used in some lines of manufacturing, for acids, alkali solutions, and other liquids, though having no real advantage over the rational scale. The hydrometer of Brix is so graduated that the degrees express directly the percentage of a given solid in the solution tested, and consequently any one instrument can only be applied to the specific solution for which it has been adjusted. Tables for the conversion of the various empirical scales to specific gravity will be found in compilations of chemical tables.*

Bohn† proposes to determine the relative specific gravities of liquids by measuring the heights of columns that exert an equal pressure.

The densities of most mixtures of liquids do not follow the ratio of the proportions of the constituents, the volume of the mixture being somewhat less than the sum of the constituents. The same is true of solutions of solids in liquids, except in quite dilute solutions, where up to a certain specific concentration ranging from one to five per cent of the solid, the excess of specific gravity over pure water is directly proportional to the weight of salt in solution — the equation $D_t = d_t + kP$ holding, where D is the density of the solution; d, the density of water at $t°$; P, the percentage of anhydrous salt, and k, a factor constant for the given salt.

The specific gravity of solids is less frequently called for in analysis. If the substance is sensibly porous, a distinction is to be made between the *real* and the *apparent* density — the former being that of the finely powdered substance, and the latter that of a fragment with whatever air is inclosed within its sensible pores.

If a lump of moderate size is obtainable, the most accurate method is to suspend it by a hair or fine wire from the hook of the stirrup of an analytical balance and weigh, and by the aid of the wooden bridge over the pan, again weigh when submerged in a beaker of water; the difference is the weight of an equal volume of water at the temperature of the experiment. Should the substance be soluble in water another liquid of known gravity is substituted.

Fig. 129. 1/8

For powders, Hogarth's flask, Fig. 129, a modification of the Sprengel tube, will be found convenient. Its capacity is ascertained, and the dry flask weighed before and after introduction of the powder; then partly filled with water. After boiling to remove any air adhering to the powder, the flask is filled and adjusted to the mark A, and again weighed. The specific gravity bottle for liquids may be employed, though not so conveniently.

The volume of a heavy solid in the form of fragments or nodules may be found by filling the body of a small long-necked flask and weighing, then pouring in mercury to the mark and again weighing. The volume of the solid is $V - \frac{w}{g}$ and its specific gravity $\frac{W.g}{V.g - w}$ where V is the capacity of the flask to the mark; g, the specific gravity of mercury at the temperature of the experiment; w, the weight of mercury poured into the flask; and W, the weight of the solid.‡

* Journ. Amer. Chem. Socy. 1899—199.
† Chem. News, 1888—1—83.
‡ Journ. Franklin Inst. 1899—200.

Another device is shown in Fig. 130. A ground stopper elongated to an open capillary tube, fits the glass bulb A whose bottom is drawn out to a narrow tube and connected by a rubber tube C to a narrow 10 Cc. burette D. The bulb is filled with water and raised or lowered until the surface reaches a mark B on the tube of the stopper, when the level in the burette is read. The bulb is now raised until the water recedes somewhat, the stopper is withdrawn, and the weighed fragment or fragments of the (insoluble) solid introduced. The stopper is replaced and the bulb lowered until the level of the water rises to B, and the burette again read. The difference between the two readings is the volume of the solid, and having its weight, the gravity is easily calculated.

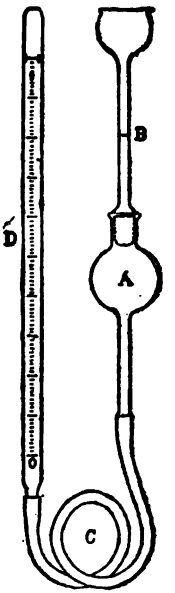

Fig. 130.

The volumenometer of Regnault-Dupre is constructed on the principle that when into a given volume of air v at normal pressure is forced another volume of air V also at normal pressure, the tension of V is increased in proportion to the ratio between v and V. Also if the volume V be reduced, as by the introduction of a solid into the vessel containing it to that extent will the tension be further increased.

A simple means of determining the gravity of a light solid in fragments is to prepare a liquid in which it is insoluble, of such a density that the solid will remain suspended, neither floating or sinking to the bottom of the vessel; then observing the density of the liquid.

Thus, raw coffee-beans (sp. gr. 1.041 to 1.368) may be thrown into a strong solution of calcium chloride, this lightened with water until the berries just sink below the surface. For roasted coffee (sp. gr. .500 to .635) the lightest grade of gasoline is adjusted with kerosene. Fresenius and Schultze recommend that a fat or wax be melted and the fluid dropped into cold alcohol; after twenty-four hours several of the globules are transferred to dilute alcohol followed by the addition of water or strong alcohol as needed. The liquid is filtered and its density determined by the alcoholometer. Drops containing air-bubbles behave differently from the others and are rejected. Fibrous bodies are tested under reduced atmospheric pressure to eliminate the air contained in the open pores.

Blyth has proposed to approximately determine quantities of the alkaloids or their salts too minute for weighing (such as are obtained in toxicological examinations) by crystallizing and measuring the crystals under the microscope with the aid of a micrometer. Knowing the crystalline form and specific gravity it is a simple mathematical problem to compute the volume and weight.

A fair approach to the proportion of a solid or liquid in an aqueous solution can often be reached by a calculation from the decrease or increase in density of the solvent due to the elimination of the solute by precipitation or evaporation, or by a change in chemical combination. The presence of other bodies remaining in the solution does not interfere. This principle has many analytical applications.

Examples are these. For the determination of tannin in an aqueous extract of oak-bark, the specific gravity of the extract is observed, and the tannin precipitated from a measured volume by cupric oxide; after filtering, the gravity is again observed. The difference between the two is compared with a table drawn up from the results of direct experiments on the purest tannin obtainable. Similarly, the density of a mixture of alcohol and water increases in proportion as the alcohol is dissipated by boiling, and the percentage of alcohol in the mixture can be calculated from a second density determination made after replacing the liquid evaporated by an equal volume of water. Urine (average specific gravity 1.020) containing albumen (specific gravity 1.314) is of a lower gravity after the albumen has been removed by coagulation and filtering. A dilute acid, such as vinegar, on shaking with (insoluble) calcium carbonate, takes into solution an equivalent of calcium and the density is increased proportionally.

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Instead of the usual procedure of drying and weighing a precipitate, it may, after thorough washing, be rinsed with water into a specific gravity flask, water added to the mark, and the flask weighed. Obviously the difference between this weight and that of the flask filled with pure water at the same temperature is that of the precipitate less the weight of an equal volume of water. Or if the precipitate is of such a nature that it will remain for a time uniformly diffused in the liquid in which it has been formed, from the difference in specific gravity of the liquid before and after clarification may be calculated the weight of the precipitate, assuming that its specific gravity has been previously determined. The formula for densimetric methods is $W = S\frac{G-g}{S-s}$ where W is the weight of the precipitate; S, the specific gravity of the precipitate; s, the specific gravity of the solution (or water) in which the precipitate is suspended; G, the total weight of the picnometer, solution and precipitate; and g, the weight of the picnometer filled with the clear solution.

The purity of a given sample of a commercial article can sometimes be judged by determining the gravity at several different temperatures, considerable variations being shown by adulterated samples as the temperature is raised, though at ordinary temperatures there may be no marked difference between the pure and adulterated. And where a certain minimum or maximum density characterizes an article of standard quality, a gravity determination alone will indicate the grade more or less accurately. Similarly, the proportion of impurities in a fairly pure commercial compound, both being freely soluble in some liquid, can be determined by making a saturated solution at a given temperature and noting the variation in gravity from that of a saturated solution of the pure compound at the same temperature. But in many cases, changes in constitution, such as through fermentation and concentration by evaporation, that may follow age or exposure, may considerably alter the normal gravity.

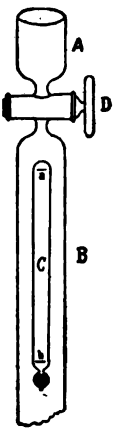

Fig. 131.

The specific gravity of a mixture of gases is determined by weighing the gas in a glass globe (page 38), and comparing the weight with that of pure air or hydrogen under similar conditions.

A method sometimes applied to illuminating gases, is based on the law that gases transfuse through a small orifice at rates proportional to the square roots of their densities. A simple apparatus for the purpose is shown in Fig. 131. A glass tube A B is closed air-tight at the top by a thin platinum plate perforated at the center by a hole .1 Mm. in diameter. The lower end of the tube is open. A glass float C slides in the tube and has two marks at the extremities a and b. The tube is lowered into a jar of mercury and filled with the gas to be tested; the stopcock D is opened until the float rises so far that the mark a coincides with the surface of mercury outside the tube. The gas is now under a pressure p. During a time t, so much gas has effused that the mark b coincides with the surface of mercury, the gas being now at a pressure p'. From another experiment with hydrogen or air, the density of the gas is easily calculated.*

* Electrical Engr. 25—311.

MELTING AND CONGEALING POINTS.

Determinations by the temperatures of liquefaction and solidification after fusion are practically restricted to bodies that melt and congeal at comparatively low temperatures, such as the fats, fatty acids, waxes, etc.

Where a reasonably large quantity of the substance to be tested is at hand, twenty grams or more is placed in a beaker provided with an arrangement for continuous stirring and an accurate thermometer. The beaker is set in another containing water or oil heated a little above the melting point of the substance. As soon as partial fusion takes place the stirrer is rapidly turned; so long as some of the substance remains unfused the thermometer will remain stationary at the melting point.

For paraffin and like bodies, Kissling * recommends to heat a quantity in a covered beaker to ten degrees above the melting point, then surround the beaker with an air-jacket in the form of an open glass cylinder. The paraffin is allowed to cool slowly while stirring with a thermometer, until a thin skin forms on the surface and bottom of the liquid and it becomes cloudy. This temperature is taken as the melting point.

Where the quantity of substance available for the test is limited, or when it is desirable for other reasons to use only a small amount, the above process will not answer, and several plans suited to the reduced quantity have been proposed. Most of these assume the melting point to be the temperature at which some physical alteration denoting incipient or entire fusion becomes apparent; for example, when a disk of the solid becomes spherical, a globule transparent, a layer softens so far as to yield to a given continuous uniform pressure, or the edges of a cube become rounded. Since there is always a small, sometimes a great difference in the melting point obtained by methods of this class, whenever a melting point is stated there should always be appended a note of the method used for the determination.

1. A short glass tube of narrow bore is filled with the melted substance by suction; after cooling and remaining solid for a sufficient period, the tube is tied to a delicate thermometer and the two lowered into a beaker of water, which is then heated slowly on the water bath. The temperature is observed when the contents of the tube become transparent. For powders, the tube is closed at the bottom and the point of liquefaction observed. Somewhat different results are obtained with tubes of different diameters of bore.†

2. A drop of the melted fat may be placed on a globule of mercury contained in a porcelain crucible. When the fat has solidified, the crucible is floated in a dish of water and a delicate thermometer inserted in the mercury. The water is slowly warmed until the fat spreads over the surface of the mercury; the reading of the thermometer at this moment is taken as the melting point.

3. Wiley recommends to drop a melted fat on a cake of ice, the drops congealing to form disks of a uniform size. A test-tube is half filled with water, then nearly filled with alcohol, retaining their integrity as far as may be. Near the junction is a point where the specific gravity of the somewhat diffused liquids is the same as that of the fat, and consequently the disks will remain suspended at that point. One of the disks is dropped into the tube and a delicate thermometer suspended close to it, and the tube heated in a water bath until the disk, after shriveling, becomes spheroidal. Precautions must be taken against air bubbles attaching to the disk, and to prevent the disk touching the side of the tube.

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* Journ. Socy. Chem. Ind. 1898—380.

† Allen, Coml. Org. Anal. 3—2—520.

With oils that remain liquid below zero, disks are made by dropping the oil into a glass spoon that has been chilled by solid carbon dioxide. A disk is then dropped into a test-tube containing a lower layer of a mixture of concentrated sulfuric acid and abolute alcohol, and an upper layer of absolute alcohol floating on the lower. The disk remains suspended at some point in the lower layer. The tube is immersed in a beaker of alcohol cooled by solid carbon dioxide in a surrounding beaker, this jacketed by a third beaker containing a little concentrated sulfuric acid to prevent clouding by deposition of frost. The carbon dioxide is removed when the test-tube has become of the temperature of the surrounding alcohol, and the latter allowed to rise in temperature while being constantly stirred.

4. Damien, by means of a special apparatus, heats a layer of a fat to slightly above the melting point, then cools one-half the layer until it just solidifies. The change is shown by contrast of the melted and congealed halves, and the mean of two thermometers, one in each part, is taken as the melting point.

5. In several apparatus the melting point is indicated by the closing of an electric circuit. In one, the bend of a small U-tube is filled with the melted fat which is then allowed to solidify. Two platinum wires whose inner ends are nearly in contact are sealed in one limb near the bottom, and each wire connected to the pole of a galvanic battery in circuit with an electric bell. Into the other limb of the U-tube is poured a quantity of mercury. The U-tube is slowly heated in a water bath, and when the fat melts the mercury flows into the other limb and makes an electrical contact between the wires, completing the circuit and causing the bell to ring.

6. The temperature at which a disk of a fat liquefies sufficiently to stain paper on which it rests has been proposed at the melting point. In the apparatus designed, the stain is observed in an inclined mirror stationed below the paper, the disk heated by a water-bath.*

In general a simple chemical compound passes sharply from the solid to the liquid state and the reverse, while mixtures exhibit a more or less prolonged transition period. The interval of semi-fluidity is well marked with certain complex fats and preparations from them. In the case of alloys and amalgams it is probable that their bases are certain eutechtic compounds of two metals admixed with an excess of one of the metals, and the difference in melting points between them gives rise to anomalous results.

Whatever method of determining the melting point be adopted it is to be remembered that the melting point of a fat or fatty acid may be altered as much as several degrees by a previous melting, and the original figure is regained only after standing several hours after solidification.

As to whether the melting point of a given mixture is the mean of the melting points of the several constituents can only be determined by direct experiment. Thus, mixtures of butter-fat with oleo-oil or neutral lard or both, show melting points agreeing with the calculated values; while mixtures of solid fatty acids, as stearic and palmitic, have, in certain relative proportions, a lower melting point than either constituent.

The point of solidification after melting generally differs somewhat from the fusing point, as from a disengagement of the latent heat of fusion, a recalescence takes place, the thermometer remaining stationary for a few moments, or even rising a degree or more.

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* Analyst, 1899–84.

The determination has been applied to various mixtures of analogous compounds. Thus, for the determination of paratoluidin in commercial toluids, Raabe adds a weighed quantity of pure paratoluidin in such an amount as will give a mixture whose congealing point can be readily determined. The thermometer is graduated in twentieths of a degree from 30° to 60°, each twentieth corresponding to .2 of one per cent of paratoluidin. Standards are made up conforming to the usual composition of commercial samples, and their congealing points observed.

According to Pickering,* out of many thousands of compounds that have been investigated, there are but one or two in which the addition of another body has been found to raise the congealing point of a liquid; in all other cases it is lowered. Finkener † states that on warming a mixture of chemically pure substances of different melting points, which have no chemical action on each other except solvent action, the temperature remains almost constant about the melting point of the lower melting constituent until this has ceased to dissolve the more solid constituent, and then rapidly rises.

POLARIZED LIGHT.

The polariscope has a limited use in pathological examinations, determination of the alkaloids, camphors, oils, etc.; while apparatus of special design are extensively employed for the determination of the sugars.

The simplest form of polariscope is that devised by Mitscherlich, Fig. 132. A is a source of monochromatic light, a Bunsen burner whose flame impinges on a bead of sodium chloride. The rays pass through a calcite prism B by which the light is polarized, so constructed that the extraordinary ray is extinguished while the ordinary ray proceeds through a lens into the analyzer C. This is another prism so mounted that it may be rotated on its long axis by moving the arm D. The angle of rotation is shown on the vernier of the scale F divided into degrees. When the vernier points to 0° or 180° on the scale, the light transmitted to the eye at G is at a minimum; on rotating the analyzer C the light gradually increases until at 90° or 270° it is at a maximum.

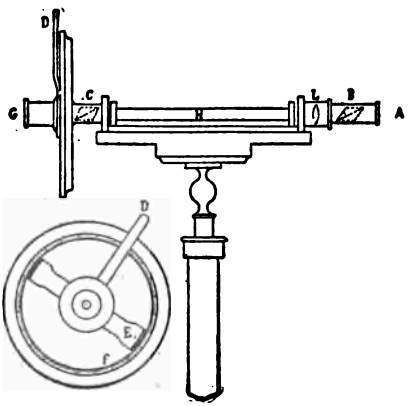

Fig. 132.

If now a tube H of standard length whose ends are closed by glass plates be filled with an optically active solution, as of a sugar, and interposed between the polarizer and analyzer, the plane of the light coming from the polarizer is turned to an extent determined by the concentration of the solution, and the point of minimum brightness is no longer at 0° or 180°, but at some intermediate division. Knowing by calculation or previous experiments to what extent the ray is deviated by a sugar solution of given strength, it is easy to calculate the weight of sugar in the tube.

Several greatly improved forms of the polariscope have been invented, principally for the determination of sugar and known as saccharimeters. In these

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* Chem. News, 1892—1—50; *Idem*, 1892—2—109.
† Analyst, 1899—269.

the reading point is shown by the identity in tint of two luminous adjacent semi-circles, the appearance or disappearance of black bands on an illuminated field, etc. A full description of these will be found in works on the polariscope and sugar analysis.

The specific rotary power of a body is the angular deviation produced when the ray passes through an optically active substance in a solution of a concentration of one gram per cubic centimeter, and of a length of one decimeter. The amount of rotation depends on the nature of the substance and the solvent, the length of the column of liquid, the temperature, and the kind of monochromatic light employed. If $(a)_D$ represents the specific rotary power of a solution with the D or sodium light; a, the angular displacement of the ray; l, the length of the column of liquid expressed in decimeters; d, the specific gravity of the solution; and p, the percentage of the solid in the solution by weight, then

$$(a)_D = \frac{100\,a}{l.\,p.\,d.}$$

SPECTRUM ANALYSIS.

Although originated many years ago and revived and improved from time to time, and apparently capable of practical application in many examinations, for several reasons none of the methods have come into practical use. Most of the processes have been devised for the alkalies, some for the analysis of the coal-tar colors, the valuation of commercial indigo,† the determination of the haemoglobin of blood, etc.

The method of Vierordt depends on the principle that if the slit of a spectroscope be divided transversely in halves, each independently adjustable, the intensity of the two spectra formed from one source of light is proportional to the widths of the slits; and if separate lights enter the slits and the widths of these be so adjusted that the intensities of the spectra are equal, then the intensities of the lights are proportional to the widths of the slits.

The apparatus used is the universal spectroscope of Kruess. The halves of the divided slit are each provided with an accurate measuring apparatus. In front of the slits is placed a flat glass cell with parallel sides containing the liquid to be examined. The upper half of the cell is eleven millimeters between the sides, the lower half (reduced by the insertion of a block of glass ten millimeters thick) only one millimeter between the sides. On adjusting the openings of the slits until the spectra are of the same brightness, the ratio between the widths of the slits is the intensity of the light emerging from a layer of the liquid ten millimeters in thickness, the intensity of the original light expressed as unity. From the ratio is calculated the 'extinction coefficient' which is defined as the "reciprocal value of the thickness which a substance must have in order to decrease the intensity of the light which passes through it to one-tenth of the original intensity." In the case of solutions the extinction coefficient depends on the concentration c of the solution.

Truchott's method differs from the above in that the brightness and duration of the spectra are compared when definite quantities of a solution of an alkali salt and one of a standard solution of the pure salt are brought into a Bunsen flame. The comparison may be made by diluting each solution to the extinction of the brightest lines. Another plan is to add from a burette to a measured

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* Thorp, Dict. Applied Chem. 3—345.

volume of pure water small quantities of a weak standard solution of the metallic compound to be determined, until a characteristic line of the spectrum just appears; then repeat with the solution to be examined. The standard solution should also contain approximately the same amount of associated metals as are in the sample to be tested.

REFRACTIVE INDEX OF LIGHT.

For measuring the specific refraction of light by liquids, various instruments known as 'refractometers' have been invented. Some of these are adapted to any refracting body, others are constructed with special reference to the examination of a certain liquid, such as the 'butyro-refractometer' for butter-fat.

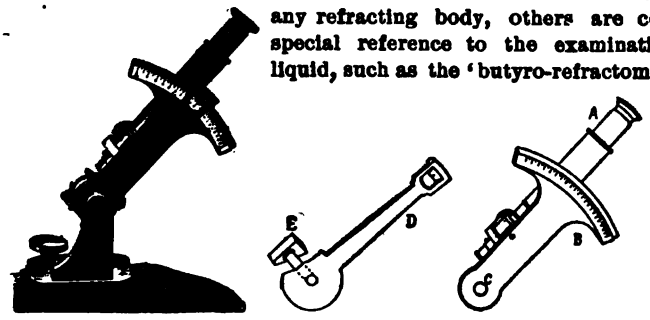

Fig. 133.

The refractometer of Abbe, Fig. 133, has a double prism E cut obliquely, between whose inclined faces is held a layer of the liquid to be tested. The prism moves in an arc with the vernier D. A telescope A is attached to the alhidade B and moves with it in the same arc as the vernier. Monocromatic light is reflected from a mirror through the prism into the telescope. If a liquid of a smaller refractive index than the glass of the prism be inclosed therein, then for a certain position of E as regards A, one-half the field appears dark, the other half light. The refractive index is read directly on the scale of the alhidade. If white instead of monochromatic light is the illuminant, the dividing line of the field is colored (due to dispersion), and must be made to appear sharp and colorless by the adjustment of a compensating apparatus.

The refractive index of a body is expressed by the quotient of the sine of the angle of the ray incident to the body divided by the sine of the refracted ray.

According to Gladstone molecular refraction and dispersion may be safely deduced from the substance in solution where the solvent is chemically inactive, but that in the case of water (refractive index at 20° for sodium light 1.3329) there is some profound change effected upon the constitution of hydracids, haloid salts, and probably some other compounds by the action of solution. Although the rule holds that a solid when dissolved retains its former refractive power, there are some exceptions.

Marked differences are found in the refractions of different varieties of the fixed and essential oils, but the data are somewhat conflicting since the refractive index is modified by the age of the oil, process of refining, the presence of free fatty acids and oxidation products, etc.

CAPILLARY ASCENT OF LIQUIDS.

The rise of a liquid in a capillary tube is observed in an instrument known as the capillarimeter. As shown in Fig. 134, it is a capillary tube BB, 150 to 200 Mm. in length, fixed to a scale A graduated in half-millimeters. The radius of the bore of the tube is determined by introducing threads of mercury, measuring their lengths, and taking their weights; the radius should be uniform throughout.

Fig. 134.

The scale is fixed in a vertical position over a dish of the liquid to be tested and lowered until the points a and a' (the zero of the scale) just touch the surface of the liquid. By means of a rubber tube slipped over the upper end of the capillary tube the liquid is drawn up a few centimeters above the final position of the meniscus of the liquid, then allowed to recede till stationary, and the height read on the scale.

The capillarimeter has been applied to the determination of alcohol in spirits, and to mixtures of the alcohols. According to Traube, the minor constituents of fusel oil and various aldehyds reduce the ascent to a greater degree than ethyl alcohol but less than amyl alcohol.

It is said that of solutions of equal concentration of some homologous series of organic bodies, the height of the rise is inversely proportional to the molecular weight of the members.

Paterson utilizes the difference in capillary adhesion for the detection of the various coloring matters of a mixture. When a dilute solution of the dye is dropped on filter paper a simple coloring matter forms a homogeneous blot, but if complex there are formed concentric rings. Taking for a basis water as 100, the speed of diffusion of solution of acid magenta is 100; of uranin is 78.5; of rhodamin is 42.8; of methyl violet is 14.2, etc.

VISCOSITY.

The viscosity or internal friction of a liquid is generally measured by the time required for a standard volume at a standard temperature to flow through an orifice of standard area. Usually the viscosity is referred to that of pure water under the same conditions, determined in the same instrument.

Applications are mainly to the fixed and essential oils, though usually in a qualitative way only or as a criterion of the lubricating quality of the former; and to the potash soaps made up from standard weights of saponifiable oils acted on by a standard volume of lye of a given concentration.

Of gum arabic and gum tragacanth,* ten per cent solutions are compared with similar solutions freshly made up of the best quality of these gums as standards. Lunge† has devised a form of viscosimeter for mucilage of tragacanth and gum thickenings; it resembles a hydrometer, and the viscosity is determined by the number of minutes required for the instrument to sink to a mark on the stem, it having previously been dipped in the solution, but it is doubtful whether reliance can be placed on an estimation of the proportion of an impurity, or that the process is capable of giving more than an idea as to the relative quality of two samples.

Prollius states that the viscosity of solutions of isinglass of a concentration of one part

* Allen, Coml. Org. Anal. 1—428 and 4—488.

† Journ. Socy. Dyers & Col. 1896—12.

in ninety parts of water ranges from 360 to 507 seconds according to the quality of the samples tested, when measured by the same instrument.

The viscosity of milk is a fairly constant value, diminished by watering and fermentation.

VAPOR TEMPERATURE.

The temperature of the vapor of a mixture of two liquids lies between those of the constituents. For the determination of alcohol in beverages an instrument known as the ebulliometer has come into considerable use in some European countries, based on the principle that steam at atmospheric pressure has normally a temperature of 100°, while the vapor of alcohol at the same pressure is only at 78.4°, and that of a spirit is in proportion to the alcoholic strength.

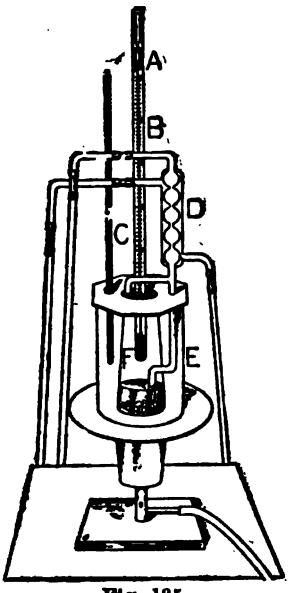

Fig. 135.

A recent form of apparatus * is shown in Fig. 135. The flask F holds the spirit to be tested; through the cork passes a delicate thermometer B graduated from 95° near the bulb to 100° at the top, and also a tube entering the condenser D. To the lower end of D is joined a tube E entering the flask, the end dipping below the surface of the liquid. To prevent cooling of the flask by draughts of air it is surrounded by a glass cylinder covered with a rubber plate carrying a thermometer.

The apparatus being connected as shown, the spirit in F is heated to boiling, the vapor of alcohol and water emitted passing through C into D where it is condensed and returns through E to F. When the thermometer has reached 90°, B is read and the temperature corrected for any variation of barometric pressure from the normal at the time of reading.

The temperature of the vapor of a spirit is depressed from that of pure water by .8° Cent. for each per cent by volume of alcohol contained in the spirit, this ratio holding good up to five per cent of alcohol. Wines or liquors above this strength are best diluted before testing. If acetic acid in any great proportion is contained a previous distillation with caustic potash is advised.

PENETRABILITY.

The resistance of a solid or semi-liquid body to penetration is occasionally applied in analysis, principally to the fats and fatty acids. The 'oleogrammeter' of Brullé † is a vertical metal rod, surmounted by a scale-pan, which slides freely in a guide-ring. The lower flat end of the rod presses on the fat to be tested brought to a temperature of 21°. The scale-pan is weighted with increasing loads until the rod penetrates the fat.

Under a rod of standard diameter, pure butter fat yields to a weight of 250 grams while margarine requires 5,000 grams, and intermediate figures obtained with mixtures of the

* Journ. Amer. Chem. Socy. 1896—1063.

† Chem. News, 1898—2—2.

two are said to allow an approximate calculation, except for mixtures containing seed oils, which greatly modify the resistance. Olive oil is tested for adulteration with cottonseed oil by first freezing the sample thoroughly; genuine olive oil yields under 1,700 grams and cottonseed oil under 1,000 grams.

The relative hardness of alloys of certain metals is observed by an apparatus which is essentially a diamond fixed to the beam of a balance, ruling lines to be measured in the microscope by a micrometer. Alloys of copper and tin show a hardness of 364 units when composed of 17 per cent of copper with 83 per cent of tin, rising to 1100 units at 75 per cent of copper with 25 per cent of tin, thence decreasing to 675 units at 96 per cent of copper with 4 per cent of tin.

The temperature to which a fat must be heated so that a glass bulb of specified weight and dimensions will sink therein has been termed the 'sinking point.' For butter-fat the bulb is pear-shaped, has a volume of one cubic centimeter and a specific gravity of 2.4. Hehner and Angell found the average sinking point of butter-fat to be 35.5°; of lard, 43°; and of beef-tallow, 50.6°, mixtures following the usual formulae.

Hassell* calls the 'rising point' the temperature at which a bulb of .5 cubic centimeters volume and .18 gram in weight will rise in a previously solidified fat contained in a test-tube one-third inch in diameter by four inches in height heated in a water-bath.

VOLTAIC ENERGY.

For a determination of a salt in aqueous solution, Gore† proposes to measure the energy excited in a galvanic couple of platinum and zinc, referred to a standard of that excited in pure water, both at atmospheric temperatures. The plates immersed in the liquid to be tested are connected with a delicate galvanometer, then the solution diluted until the voltaic current generated is sufficient only to visibly move the needle, the volume of the diluted solution being directly as the weight of salt contained. The results on mineral acids, ammonia, sodium chloride and sodium carbonate up to ten per cent solutions agreed fairly well with the determinations by specific gravity and chemical analysis, and the method is claimed to be quick and easy, and to require less substance than other analytical methods.

ADHESION.

Certain pure essential oils when treated with concentrated sulfuric acid pass to a viscid liquid, later to a viscous solid of a definite adhesiveness. The common adulterants of these oils lessen the adhesiveness directly, since they do not solidify. To determine the approximate proportion of an adulterant it has been suggested‡ to place .020 to .030 gram of the sample on a ground-glass plate and mix with one drop of concentrated sulfuric acid. A glass rod whose lower end has been ground flat, is hung from a balance-beam and counterpoised, and the end brought into contact with the mixture on the plate. The minimum weight in the opposite pan that will lift the rod is a measure of the adhesion and consequently of the purity of the oil.

FLASH POINT.

The temperature at which a mixture of the vapor of a volatile liquid and air will ignite when brought in contact with a flamelet is called the flash point. Mixtures of two liquids, the vapor of one inflammable, the other not, show a flash point varying inversely with the proportion of the former in the mixture, but only approximate results can usually be obtained by this process. For example, the flashing temperature in degrees Cent. of a mixture of alcohol and water,§ A being the percentage of alcohol, and t° the flash point.

A.	100	90	80	70	60	50	40	30	20	10	5	A
t°.	12.	16.5	19.	21.	22.3	24	26.3	29.5	36.8	49	62.	t°.

* Prescott Coml. Org. Anal. 265.

† Chem. News, 1889—1—243.

‡ Odorographia, 374.

§ Analyst, 1899—182.

Other physical constants that have been proposed are electrical conductivity and resistance, vapor density, conduction of heat, thermal expansion, cryoscopy, etc.

CHEMICAL METHODS.

The proportions of two bodies in a homogeneous mixture can be determined without separation by finding the united weights of a common constituent and calculating from the usual formula—

$$X = 100\frac{d-b}{a-b} \text{ and } Y = 100\frac{d-a}{b-a} = 100 - X.$$

where X and Y are respectively the weights in grams in 100 grams of the mixture of A and B; a and b, the proportions of a common constituent of A and B in one gram; and d the proportion of the common constituent in one gram of the mixture. Several cases are presented.

1. When each member of the mixture contains a known definite proportion of a common constituent, the proportions being unequal. The above formulae apply for the calculation, and the greater the divergence in the ratios of the constituents to the bodies themselves, the more nearly will the result of a determination approach the truth, other conditions being the same.

The same principle covers cases where a certain extrinsic associate accompanies each body in a reasonably constant proportion—such as are sometimes found in commercial articles and natural products, either originally present, acquired by age or exposure, or developed during refining or other treatment in their manufacture. Of course, some doubt always attaches to a determination made on this basis.

If with a complex body M, bearing a known proportion of a constituent m, be admixed an adulterant N containing a known proportion of a constituent n which is identical with m or analytically equivalent to it, the extent of the adulteration may be calculated from the usual formula $Y = 100\frac{d-a}{b-a}$ where Y is the percentage of N in the mixture; a, the percentage of m in M; b, the percentage of n in N; and d, the percentage of $m+n$ in the mixture. For example, an organic substance leaving when pure 17 per cent of ash, and an adulterant leaving 88 per cent of ash; if the ash in a given mixture is 70 per cent, the percentage of N is 74.6. Where N is anhydrous mineral matter, $n = 100$.

Where a mixture has such a composition that a chemical constant is not exhibited to a degree sufficiently great to be easily measured, a weighed quantity of one of the constituents in the pure state may be added to the mixture and its effect allowed for in the calculation.

2. When both members are brought to a form that contains a common constituent. The usual formula apply to all the following cases.

A. When the proportion of the constituent in one body becomes a determinable quantity, in the other remains practically at zero. The addition of an element to one of the bodies may be done by a simple operation, *e. g.*, the conversion of an alloy of platinum and zinc to a mixture of platinum and zinc oxide, or both bodies may be brought to a different combination, then reduced to the above condition. The reverse of this may be availed at times—the withdrawal of a common constituent from one of the bodies, leaving the constituent in the other body in the original amount; or, when only one of the bodies contains a constituent that can be wholly expelled.

B. When the constituent is introduced into both bodies to a measurable though differing proportion, the general formula applies. Frequently the in-

crease in weight or volume alone will furnish an easy means of determination: the absorption of a halogen or oxygen by certain oils is an example. Otherwise, as when an acid radical is replaced by another (*e. g.*, a metal with an organic radical changed to a carbonate), a simple calculation is required. As in A, the complete removal of a common constituent from both bodies may be made the basis for a determination.

Basic radicals, difficult of direct separation, may be combined with one acid radical, and acid radicals with one base; thus, valeric and acetic radicals with barium, barium valerate containing 40.41 per cent of barium, and barium acetate, 58.72 per cent.

3. By the action of a reagent there is produced with or from both members a third body that can be separated and determined. This is usually a precipitate, but may be a gas, as where two carbonates are treated by hydrochloric acid and the evolved carbon dioxide caught and weighed.

4. With a mixture of two bodies having an element or radical in common, the proportion may be calculated from the increase or decrease in weight when one body is transformed to the composition of the other. Thus ferrous oxide with ferric oxide, lead sesquioxide with lead protoxide, tungsten with tungstic acid, cupric oxide with metallic copper—in each case one being oxidized or reduced to the composition of the other.

The usual formula applies, a being the theoretical weight were the percentage of the transformable constituent 100; b, the original weight of the mixture; and d, the weight after transformation.

Even the combination of both bodies may be changed to other dissimilar forms, as an alloy of silver and copper to silver nitrate mixed with cupric oxide. Owing, however, to the uncertainty that each body is brought entirely to the presumed condition, the method is but seldom used.

5. Where the two bodies react with a third but in unlike ratios: *e. g.*, one part of methyl alcohol reduces 9.22 parts of potassium bichromate; one of ethyl alcohol, 4.28 parts; and one of propyl alcohol, 3.28 parts.

The two mixed bodies may each react with a reagent but a certain determinable product be formed from only one. For example, dinitro-phenol and picric acid when acted on by bromine are transformed according to the equations—

$$C_6H_3(NO_2)_2OH + Br_2 = C_6H_2Br(NO_2)_2OH + HBr.$$
$$C_6H_2(NO_2)_2OH + Br_2 + H_2O = C_6H_2Br(NO_2)_2OH + HBr + HNO_3.$$

both reacting to form bromo-dinitrophenol and hydrobromic acid, but picric acid yielding also nitric acid. The determination of the nitric acid is the basis of a method for the organic mixture.

In volumetric analysis, a mixture of two bodies reacting in unlike ratios to the titrand may be determined in one titration. In the formula a is the volume in cubic centimeters reacting with one gram of X, and b and d the corresponding volumes for Y and the mixture. An example is the titration of a mixture of potassium and sodium hydrates by a standard acid.

The combining weights of organic acids and bases are often made the basis of their determinations. Thus the saponification equivalent (page 240) of oils; usually saponifiable fats and oils have nearly the same equivalent, but the mineral and rosin oils have comparatively low figures, and mixtures of one of these with a fat oil may be quite accurately determined. The proportions of one of the elementary constituents of organic bodies may sometimes be used, but as a rule in such analogous bodies as are likely to be found together there is so little variance in the proportions of any one element that the results are but approximations.

Solubility. The proportions of a mixture can be calculated from the coefficients of solubility at a given temperature in a simple solvent or a solution of a given concentration. Obviously, this method is more practicable with solvents that exhibit an apparent chemical reaction with the bodies than if the solution is but a simple one, since with the latter a prolonged digestion is needed. In any case the process is empirical, as the solvent power of a liquid for one body is altered by the presence of the other.

By the rate of solubility of a third body in a mixture of two liquids simple or complex. As examples, the difference in solubility of dry cinchonine in alcohol and in chloroform is a basis for the determination of small amounts of the former liquid in the latter; zein (a proteid of maize) is practically insoluble in water and in alcohol, but dissolves in a mixture of the two according to their relative proportions. Isoterebenthene absorbs (at 24° and 734 Mm. of mercury) 34 per cent of gaseous hydrochloric acid, while metaterebenthene absorbs only 17.7 per cent under the same conditions; similarly, one volume of oil of turpentine absorbs 7.5 volumes of ammonia at 16° Cent., while one volume of oil of lavender absorbs 49 volumes. Glycerol mixes with water to a clear liquid in all proportions, but if to commercial glycerin containing water is added a certain weight of anhydrous phenol, the mixture becomes turbid on the addition of water beyond a certain proportion, the amount varying inversely with the water-content of the original glycerin. A mixture of acetic and formic acids boiled with water and yellow mercuric oxide takes up mercury equivalent to the acetic acid only.

Two liquids immiscible or nearly so at ordinary temperatures and pressures coalesce to a homogeneous mixture at a given higher temperature and pressure called by Crismer "the critical temperature of dissolution." He has applied the principle to the determination of mixtures of certain fats.

6. Where a chemical reaction originates a measurable physical attribute in one or both members. The most common of these are the exothermic reactions of various organic bodies when treated with certain reagents, such as concentrated sulfuric acid, sulfur chloride, or bromine. Where the specific rise in temperature is great enough to be measured by an ordinary thermometer the process furnishes a simple practical test, though the results are but approximate at best. An example is the determination of monomethylamin in commercial dimethylanilin; on treatment with an equal volume of acetic anhydride there is a rise of about .82° Cent. for each unit of monomethylamin in the mixture; but, as in most other mixtures, the constant applies only through a limited range in the proportions of the mixtures and in the absence of certain common associates.

The heat of combustion of the animal and vegetable oils ranges from 8835 to 10797 calories as determined in the Atwater-Blakeslee calorimeter, the sperm, rosin and mineral oils showing considerably higher values than the fatty oils.*

When for any reason the chemical reaction is slow or incomplete with the proportions of the constituents of a given mixture, the observation can often be facilitated by incorporating a weighed amount of one constituent or a passive diluent. The calculation is then as follows: given the weight of the original mixture W; the weight of the diluent added, w; and the constant of the compounded mixture d'; then Y', the percentage of B in the latter is found from the equation $Y' = 100\,\frac{d' - a}{b - a}$; and Y, the percentage of B in the original mixture, is $Y = Y'\,\frac{W + w}{W}$.

* Journ. Amer. Chem. Socy. 1901—170.

CHAPTER 8.

THE CALCULATION OF ANALYSES.

The results of analyses are expressed decimally for uniformity and ease of comparison with others of the same kind. A few exceptions are met with, as in reporting an assay of gold ore, where the value in dollars per ton of ore is given, or a natural water in grains per gallon or parts per million.

Percentages always refer to 100 parts by weight of a solid, and also of a liquid unless volumes are specified. Should the constituents of a liquid be stated as grams per liter or grains per gallon, the specific gravity of the liquid should also be recorded to allow a recalculation to weight, if desired for comparison with other analyses so expressed. Many commercial solutions, however, have practically the same gravity as water, and others vary but little from a well-known specific standard.

Gas analyses are stated either as volumes per hundred or in percentages by weight or both. Either one can easily be calculated from the other.

In reporting a result it is the custom to follow the general rule of investigators that only the extreme right-hand digit may be inaccurate. This in most analyses is considered to be the second beyond the decimal point, though often the tenth or even the unit figures may not be above suspicion. On the other hand, if the proportion of a constituent be very small and the method for its determination exceptionally accurate, the result may with propriety be extended to as many as four or five places of decimals; *e. g.*, in the following analysis of bar lead.

Arsenic	trace	Iron	.00496
Antimony	.00847	Zinc	.00517
Silver	.00105	Nickel	.00125
Copper	.00946	Lead (by difference)	99.97464

But in all ordinary analyses of substances whose constituents are contained in considerable proportions, where results are reported to the fourth or fifth place of decimals, the absurdity warrants a suspicion of the competence of the chemist if not of charlatanry.

In many analyses one is at liberty to tabulate the results either as elements, radicals, molecules or compounds, and as these are calculated one from another by stoichoimetrical rules there can be no preference on the score of numerical accuracy. Some authorities would adopt the first form exclusively—that in every analysis there be reported the elements uncombined, as in this way the chemist inclines to no particular theory as to the manner in which they are associated. As carrying out this principle literally would mean the exclusion of most proximate analyses, we must presume it intended to apply only to a single class of analyses whose purpose is to fix the elementary constitution of pure chemical compounds, and as a protest against grouping elements in a manner not sanctioned by modern theories.

In technical analysis, where the subject is a raw material or its products or a commercial article, the adoption of such a course would greatly lessen the intelligibility of the larger number of analyses, more especially as they are

usually intended for the information of those seldom so versed in chemistry as to be able to infer the molecular structure from a report of the uncombined elements. For to the extent that an analysis is to be an arbiter of the fitness or value for a particular use or to describe the general character of a substance, that form of a report conveying this information in the fullest and clearest manner is certainly to be preferred, irrespective of its accordance with the views held at present regarding molecular structure and dissociation. With minerals, ores, and inorganic bodies generally, the metals and metalloids have heretofore been combined with oxygen, the halogens, etc., and this practice is likely to be retained for some time to come, since as one or another of these known or assumed compounds predominates, it will often impress its individual characteristics and valuable or detrimental properties on the substance of which it forms a part.

All things considered, as a rule it seems best, at least in technical analyses, to report the elements or radicals combined into such molecules as exist in the substance under examination, inferring this from its origin or general character or by qualitative tests; lacking this information they may be set down as ions or elements as seems best suited for the purpose for which the analysis is to be employed.

If the results of two or more determinations of a constituent of a material agree fairly well, the average of the two is reported. When the two results are both greater or both less than the true content, the average will be intermediate in accuracy between the two, while if there is a minus error on one and a plus error on the other, the average will usually be more accurate than either. If, however, one is known to be slightly inferior from faulty manipulation or other causes, or where there is a considerable difference between the two and in one there is known to have been incurred a considerable loss or gain, the result obtained on the other may be reported; but it is always more prudent to repeat the analysis.

In averaging the results of duplicate determinations made on unequal weights of material, the calculated *percentages* are added together and the sum divided by the number of determinations.

An indeterminate mixture of certain analogous bodies may sometimes be obtained in technical analysis, and if for any reason a separation is not practicable or not deemed of enough importance to repay the time and labor required, the mixture may be reported as composed only of the typical constituent or the one present in the greatest proportion. Clearly this is permissible only with comparatively unimportant constituents and where the custom generally obtains.

A. The computations to be made in most gravimetric analyses are two in number: first to eliminate from the formula of the precipitate as weighed all the elements except those comprised in the compound sought, and second, to reduce this remainder to parts per hundred of the substance analyzed. The following examples show this to be a very simple matter.

Having weighed 1.203 grams of a speiss and by the routine of analysis obtained all the arsenic in a precipitate which after ignition has the formula $As_2P_2O_7$ and weighs .5040 grams, to calculate the weight and percentage of arsenic in the speiss.

From the formula we find the molecular weight by multiplying the number of atoms of each element by its atomic weight:

Arsenic	2 atoms $\times$ 75 =	150
Phosphorus	2 atoms $\times$ 31 =	62
Oxygen	7 atoms $\times$ 16 =	112
Molecular weight		324

That is, in 324 parts of the precipitate there are 150 parts of arsenic, 62 parts of phosphorus, and 112 parts of oxygen. And from the proportions,

324 : 150 : :	.504 grams $As_2P_2O_7$	: X.	$X = .2333$ grams	As.
" : 62 : :	"	: Y.	$Y = .0965$ "	P.
" : 112 : :	"	: Z.	$Z = .1742$ "	O.
			.5040 "	$As_2P_2O_7$.

To reduce the above to percentage:

1.203 grams speiss : .2333 grams As : : 100 per cent : V.

$V = 19.39$ per cent of arsenic in the speiss.

In general, if a is the weight in grams of the substance taken for analysis; b, the weight of the precipitate; c, the molecular weight of b; d, the molecular weight in b of the compound sought; and X, the percentage in a of the compound sought; then $X = \frac{100.b.d}{a.c}$

The calculation may be somewhat abbreviated by the use of the decimal equivalent for $\frac{d}{c}$, of which lists for the commoner elements are to be found in books of chemical tables.* Or when several analyses of one kind are in hand, by making $a = \frac{d}{c}$, X will equal 100 b. As oftentimes this weight of sample is smaller than desirable it may be doubled or tripled and b divided by two or three accordingly. Logarithms may be used for the calculations, though here their advantage is not very evident — $(\log d + \log b) - (\log c + \log a) = \log X$; or, $\log \frac{d}{c} + \log b - \log a = \log X$.

The element or compound to be determined may not be comprehended in the precipitate weighed, as in the example given on page 13, where the following reactions are involved:

$$2(C_6H_5OH) + 2H_2SO_4 = 2(C_6H_5HSO_4) + 2H_2O \ldots\ldots\ldots\ldots 1.$$
$$2(C_6H_5HSO_4) + BaCO_3 = Ba(C_6H_5SO_4)_2 + H_2CO_3 \ldots\ldots\ldots\ldots 2.$$
$$Ba(C_6H_5SO_4)_2 + Na_2CO_3 = Na_2(C_6H_5SO_4)_2 + BaCO_3 \ldots\ldots\ldots\ldots 3.$$

The calculation is

A. $BaCO_3$, molec. wt. 197.4 contains Ba, molec. wt. 137.4.

B. Ba, molec. wt. 137.4 combines with $(C_6H_5SO_4)_2$ giving $Ba(C_6H_5SO_4)_2$ molec. wt. 483.62.

C. $Ba(C_6H_5SO_4)_2$ molec. wt. 483.62 is formed from $2(C_6H_5HSO_4)$, molec. wt. 348.236.

D. $2(C_6H_5HSO_4)$ molec. wt. 348.236 is formed from $2(C_6H_5OH)$, molec. wt. 188.096.

Hence,

E. 197.4 : 137.4 : : weight of $BaCO_3$: weight of Ba $= x$.

F. 137.4 : 483.62 : : x : weight of barium phenolsulfonate $= y$.

G. 483.62 : 348.236 : : y : weight of phenol-sulfonic acid $= z$.

H. 348.236 : 188.096 : : z : weight of phenol.

But in each of the three equations we see that two C_6H_5 groups are concerned, hence for the proportions E, F, G, and H may be substituted the simple one —

Molecular wt. of $BaCO_3$ (197.4) : twice the molec. wt. of phenol (188.096) : : weight of $BaCO_3$ found : weight of phenol sought.

Assaying. If an assay-ton (page 41) of ore is taken for the assay each milligram of metal obtained represents one ounce per ton of 2,000 pounds, or if a

* Journ. Amer. Chem. Socy. 1896—903.

grams are taken, then 29.167 times the weight of gold or silver divided by *a* equals the ounces per ton. In assaying separately the malleable scales that refuse to pass the finer seives and the powder passing through, the calculations should be made as for two separate ores and the sum of the results figured to the sum of the weights of scales and siftings.

In taking a given volume of a liquid for analysis it is often more convenient to measure than to weigh, but here the specific gravity and temperature must be taken into consideration. The weight in grams is the product of the volume in cubic centimeters multiplied by the specific gravity of the liquid, both at the temperature of the experiment.

At times, in deciding the value of a commercial article by comparison of an analysis with others of the same material, some exogenous or variable factor must be eliminated or introduced, such as moisture acquired from the air or rain. The following analyses, A and B, of two shipments of malt, are not directly comparable since one refers to the material in a moist condition as received, the other after drying; hence either A is changed to the form of B (as in a) by proportionally increasing the percentage of each element by dividing by the difference between the total and the percentage of the moisture to be eliminated; or B to the form of A, as in b, through multiplication by the same remainder.

	A.	B.	a.	b.
Sugar and carbohydrates	18.03	24.48	19.44	22.06
Starch	48.22	48.58	52.00	43.77
Cellulose, etc	9.21	9.32	9.95	8.40
Proteids	11.92	11.00	12.86	9.91
Fat	1.81	1.29	1.95	1.16
Ash	2.97	4.24	3.20	3.82
Moisture	7.28	....	....	9.90
Undetermined and loss	.56	1.09	.60	.98
	100.00	100.00	100.00	100.00
Moisture		9.90	7.28	

B. The percentage composition of a substance is derived from its formula by dividing the product of the number of atoms of each element times its atomic weight by the molecular weight of the compound and multiplying the quotients by 100. For example, the percentage composition of camphor ($C_{10}H_{16}O$) is deduced —

Carbon,	$10 \times 12.000 = 120.000$	$\times 100 \div 152.128$	$= 78.88$	per cent
Hydrogen,	$16 \times 1.008 = 16.128$	$\times$ " $\div$ "	$= 10.60$	"
Oxygen,	$1 \times 16.000 = 16.000$	$\times$ " $\div$ "	$= 10.52$	"
Molecular weight,	152.128		100.00	"

C. The empirical formula of a chemical compound is deduced from an analysis by dividing the percentage of each element by its atomic weight, and the quotients by their greatest common divisor; thus:

Carbon,	$78.88 \div 12. = 6.573$	$\div .657 = 10$	atoms.
Hydrogen,	$10.60 \div 1.008 = 10.516$	$\div$ " $= 16$	"
Oxygen,	$10.52 \div 16. = .657$	$\div$ " $= 1$	"

Hence the formula $C_{10}H_{16}O$.

Where isomorphous elements replace those constituting the compound, they are first eliminated, as in the following example of a native silicate.

Silica	62.38	Magnesia	10.37
Titanic acid	.24	Lime	.12
Alumina	26.29	Combined water	.50
Ferric oxide	.15		
		Total	100.05

It might be inferred from the analysis that the mineral is a hydrated silicate and titanate of alumina, lime, magnesia and ferric oxide, but in view of the relatively minute proportions of water and the oxides of iron, calcium and titanium, we are justified in regarding them as incidental only, and the mineral as an anhydrous compound of silica, alumina, and magnesia, the ferric oxide replacing alumina, the lime, magnesia, and the titanic acid, silica.

With this view we first eliminate the water by using as a divisor $\frac{100.05 - .50}{100} = .9955$.

Silica	62.38 +	.9955 =	62.66
Titanic acid	.24 +	" =	.24
Alumina	26.29 +	" =	26.41
Ferric oxide	.15 +	" =	.15
Magnesia	10.37 +	" =	10.42
Lime	.12 +	" =	.12
	99.55		100.00

Next we find how much alumina the .15 per cent of ferric oxide replaces and substitute it therefor:

Fe_2O_3 (mol. wt. 160) : Al_2O_3 (mol. wt. 102.2) : : .15 : X. X = .09, an 26.41 + .09 = 26.50.

Similarly we find the silica increased to 62.85, and the magnesia to 10.50 The analysis now stands

Silica,	62.85
Alumina,	26.50
Magnesia,	10.50
	99.85

Dividing the above by the molecular weights:

Silica	62.85 ÷	60.40 =	1.041
Alumina	26.50 ÷	102.20 =	.259
Magnesia	10.50 ÷	40.30 =	.261

The empirical formula is therefore $(Al_2O_3)_{.259}(MgO)_{.261}(SiO_2)_{1.041}$; or dividing by .260 and allowing for the errors of analysis, $Al_2O_3.MgO.4SiO_2$, or $\frac{Mg}{Al}>O_{12}<Si_4$.

A rational formula can only be deduced after certain additional data have been obtained.*

D. An indirect analysis is applicable for material wherein two elements whose atomic weights differ considerably each combines with a third element or compound. The calculation may be illustrated as follows: —

If we weigh one gram of metallic lead and (by solution in nitric acid, evaporation and ignition) convert it to lead protoxide, we will find the weight of the latter to be $1 \times \frac{206.92 + 16}{206.92} = 1.0773$ grams; similarly, one gram of magnesium forms $1 \times \frac{24.3 + 16}{24.3} = 1.6584$ grams of magnesium oxide. An alloy of one gram of each metal would give 2.7357 grams of the mixed oxides, and with other proportions of the metals we would find —

* Roscoe & Schorlemmer's Chemistry, 3—1—84.

Metals.			Oxides.		
Grams Pb +	Grams Mg =	Total.	Grams PbO +	Grams MgO =	Total.
2.000	None	2.000	2.1546	None	2.1546
1.999	.001	"	2.1536	.0017	2.1553
1.998	.002	"	2.1525	.0033	2.1558
1.997	.003	"	2.1514	.0050	2.1564
1.996	.004	"	2.1503	.0066	2.1569
and so on to					
None	2.000	"	None	3.3168	3.3168

Notice that the weight of the mixed oxides increases directly and uniformly with the weight of the magnesium in the alloy and inversely with that of the lead.

The above table might be extrapolated to show the exact proportion of each metal for every weight of the oxides, since a given weight of oxide can be produced from only one combination of metals, but this is superfluous since a simple calculation will answer the same purpose — for example, given the weight of the alloy 2 grams, and that of the oxides 2.3289 grams; the difference, .3289, is oxygen, and since 2 grams of lead combine with only .1546 of oxygen, the excess of .1743 gram is due to the presence of a certain weight of magnesium oxide. Now, since 1 gram of lead combines with .0773 of oxygen and 1 gram of magnesium with .6584 of oxygen, the difference, .5811, is to 1 gram of magnesium as .1743 is to the weight of magnesium in the alloy, that is to .300 gram.

In general, if X is the percentage of one metal A in the alloy, and Y the percentage of the other, B; a, the weight of the oxygen combining with 100 grams of the metal A: b, the oxygen combining with 100 grams of the metal B; and d, the found weight of oxygen combined with 100 grams of the alloy; then —

$$X = 100\,\frac{d-b}{a-b} \text{ and } Y = 100\,\frac{d-a}{b-a} = 100 - X.$$

It will be seen that the greater the difference between the atomic weights of the metals concerned, the less is the correctness of the result affected by errors of analysis.

The same principle is applied to a mixture of potassium and sodium chlorides by determining the chlorine, to barium and calcium carbonate, etc. Landis * gives the following general formulae.

Let W be the weight of a mixture of two salts; w that of the constituent common to both; x the weight of salt containing the greatest amount of common constituent, and v that containing the least; a the weight of common constituent in one gram of x, and b that in one gram of y:

$$\text{Then } x = \frac{w - bW}{a-b} \text{ and } y = \frac{w - aW}{b-a} \text{ or } W - x$$

Or if c is the molecular weight of x, and d that of y; and V the calculated weight were all the common constitutent combined with the base of Y:

$$\text{Then } x = c\,\frac{V-W}{d-c}, \text{ and } y = W - x.$$

A variation in practice is that of determining the weights of the common constituent added and of the product. Thus, a solution of potassium chloride and potassium bromide is titrated by silver nitrate, requiring of the titrand a volume containing a grams of metallic silver; the precipitated silver chloride and bromide is weighed, and the calculation made from these data. The formula $X = 100\,\frac{d-b}{a-b}$ applies, X being the percentage of potassium chloride in the mixture; a, the calculated weight of chlorine in the substance were it all potassium chloride; b, the calculated weight of bromine in the substance were

* Journ. Amer. Chem. Socy. 1896—182.

it all potassium bromide; and d, the difference between the weight of the precipitate and the weight of silver used for precipitation.

The principle may be extended to three elements combining with a fourth, as chlorine, bromine and iodine. A solution containing the elements is divided into three equal parts and each precipitated by silver nitrate. One precipitate, made up of AgCl + AgBr + AgI is weighed; the second weighed after digestion with sodium bromide by which the chlorine is replaced by bromine while the AgI is unaffected; and the third after digestion with sodium iodide which leaves the precipitate entirely composed of silver iodide.

Let x be the weight of AgCl, and a its molecular weight.
y " AgBr, " b "
z " AgI, " c "
w " AgI + AgBr + AgCl $= x + y + z$.
w' " AgI + AgBr + AgBr.
w'' " AgI + AgI + AgI,

Then

$$x = \frac{a(w' - w)}{b - a};\ y = \frac{b(w'' - w')}{c - b} - \frac{b(w' - w)}{b - a};\ \text{and}\ z = w' - \frac{b(w'' - w')}{c - b}$$

And generally, when two bodies or constituents thereof have a common physical attribute varying with the conditions of temperature, etc., the measure of the attribute in a mixture will serve as a basis for calculating the proportions of the bodies. If X is the percentage of one body A; Y, that of the other B; a', a'', a''' ....., the values of a constant of A under different conditions; b', b'', b''' ....., the corresponding values of B; and d', d'', d''' ....., the corresponding values of the mixture; then $X : Y :: b' - d' : d' - a' :: b'' - d'' : d'' - a'' ::$ etc.

A mixture containing among other constituents two having a common element or compound; the proportions of the two are calculated from the formulae —

$$X = \frac{100\,(d - b) + bZ,}{a - b} \text{ and } Y = \frac{100\,(d - a) + aZ}{b - a}$$

where X and Y are the percentages of the two constituents and Z the percentage of the remainder of the mixture; a and b, the proportions of the common element in the two constituents, and d the proportion in the mixture as found by analysis. For example, a mixture of potassium chromate, potassium bichromate, and 17 per cent of other alkali salts, analyzed 12.19 per cent of available oxygen; since potassium chromate contains 12.35 per cent, and potassium bichromate 16.30 per cent of available oxygen, the percentage of the former compound was 33.80, and of the latter 49.10 per cent.

E. Volumetric analysis — Normal solutions. To prepare a normal solution of sodium chloride (58.50 grams per liter), about 60 grams of common salt was dissolved in a liter of water, and 20 Cc. of the solution precipitated by silver nitrate —

$$NaCl\ (58.50) + AgNO_3\ (169.96) = AgCl\ (143.37) + NaNO_3.$$

giving 2.940 grams of AgCl; at this rate 1000 Cc. would give $\frac{1000}{20} \times 2.940 = 147$ grams, and the proportion of NaCl in solution is therefore 59.980 grams since 143.37 : 58.50 : : 147 : 59.980.

A normal solution should contain 58.500 grams NaCl.
This solution contains 59.981 " "

There is in excess therefore 1.481 " "

We may consider that we have a liter of strictly normal solution containing an additional 1.481 grams of NaCl, and the problem is to find in how much water this excess is to be dissolved to make it of normal strength — in other words, how much water is to be added to the liter to compensate for this extra amount of NaCl. It is 25.3 Cc., since 58.50 : 1000 : : 1.481 : 25.3.

But a portion of the original solution was used in making the test by silver nitrate, so from the remainder of the liter is measured say 950 Cc., and 24 Cc. of water added to it, since 1000 : 950 : : 25.3 : 24.

Should the original solution prove weaker than normal instead of stronger, the proper additional weight of salt to be dissolved may be ascertained by a similar calculation.

It is often convenient to make up two solutions, one slightly stronger, the other slightly weaker than normal and mix them in the proper proportions; this avoids in great measure the concentration that would follow the dilution of a strong solution with water and the correction therefor. The formula $X = 1000 \frac{d - b}{a - b}$ applies, where X is the volume of the stronger solution and $1000 - X$ that of the weaker to be united; a, the titre of the stronger solution and b, that of the weaker; and d, the concentration of a strictly normal solution. A strong solution may be diluted with water according to this formula, b being of course zero.

In most cases it will answer all purposes to make volumetric solutions only approximately normal and allow for the variation in the calculation of results. The corresponding volume of a strictly normal solution is found by multiplying the volume used in a titration by a factor obtained by dividing the actual content by the normal content.

If m represents the weight of a pure reagent to be dissolved in a liter of water to form a strictly normal solution S, then $\frac{m}{10}$ grams will exactly combine with 100 Cc. of any other normal solution S' reacting with it; but should the reagent contain impurities (of such a nature as not to react with S'), then the number of cubic centimeters of S' required expresses directly the percentage of the pure reagent. And in practice $\frac{m}{10}$ grams of a commercial substance may be dissolved and titrated; *e. g.*, when 10.792 grams of a silver-copper alloy is dissolved in nitric acid and titrated by normal sodium bromide, the number of cubic centimeters gives the percentage of silver without further calculation; though for practical reasons it would be better to dissolve 1.0792 grams and titrate by a decinormal solution.

For standardizing some solutions it may be an advantage to liberate the reacting body in situ just before the titration by means of a second standard solution. Thus, for standardizing sodium thiosulfate solution by iodine (page 129), instead of weighing the pure iodine, to a solution of an excess of potassium iodide is added a measured volume of standard potassium bichromate whose strength in terms of iron is known. The weight of the reacting body liberated is calculated as follows: If one molecule of the second solution liberates a molecular weight a of the reacting body, and also reacts with a molecular weight b of the standard; and if one Cc. of the second solution is equivalent to c grams of the standard; and the volume of the second solution used is V; then the weight of the reacting body liberated is $V \frac{c.a}{b}$. Thus, one molecule of potassium bichromate liberates six atoms of iodine from potassium iodide, and also converts six atoms of iron from the ferrous to the ferric state; if one Cc. of standard bichromate is equivalent to .0071 gram iron, then 20 Cc. would liberate $20 \times \frac{.0071 \times 76\ 1.1}{336.12} = .3217$ gram iodine.

If there be ascertained the relation between a volumetric solution and a given chemical compound, from the ratio of their combining weights may be calculated not only the corresponding relation between the solution and any radical of the compound, but also that of any other combination into which the radical may enter. For example, if one cubic centimeter of a potassium permanganate solution reacts with a grams of crystallized oxalic acid ($H_2C_2O_4 . 2H_2O$, 126.048), it is also equivalent to $a \times \frac{90.016}{126.068}$ grams of the anhydrous acid ($H_2C_2O_4$, 90.016) and to $a \times \frac{88}{126.048}$ grams of the C_2O_4 radical. And should a

precipitate of zinc oxalate be decomposed by sulfuric acid and the acid radical titrated by permanganate, each cubic centimeter of the permanganate reduced will represent $a \times \frac{65.4}{126.048}$ gram of zinc (65.4) or $a \times \frac{81.4}{126.048}$ grams of zinc oxide (81.4).

Similarly, if two or more chemical compounds A' A', A'',..... react with a volumetric solution S, and the relation between S and A is known, the relation to A', A'' ..... may be calculated. Let a be the molecular weight of A; b, the coefficient of A in the equation expressing the reaction; c, the coefficient of the molecule of the reagent of S in the equation; and w, the weight of A equivalent to one cubic centimeter of S: and let a', b', c', and w' be the corresponding values of A'; then

$$w' = \frac{w.a'.b'.c}{a.b.c'}$$

For example, in the titrations of potassium nitrite and molybdenum suboxide by potassium permanganate, the equations are

$$2K_2Mn_2O_8 + 10KNO_2 + 11H_2SO_4 = 10HNO_3 + 7K_2SO_4 + 4MnSO_4 + 6H_2O.$$
$$17K_2Mn_2O_8 + 5Mo_{12}O_{19} + 51H_2SO_4 = 60MoO_3 + 34MnSO_4 + 17K_2SO_4 + 51H_2O.$$

If one cubic centimeter of permanganate oxidizes say .007 gram of KNO_2, it is also equivalent to .00704 gram of $Mo_{12}O_{19}$, since

$$w' = \frac{.007 \times 1456 \times 5 \times 2}{85.15 \times 10 \times 17} = .00704.$$

Empirical standard solutions. To escape the tedium of lengthy calculations, these are made up to express directly the percentages of the body titrated by the number of cubic centimeters of the solution. For example, in the determination of calcium bicarbonate in the analysis of a natural water, to prepare a solution of such a strength that each cubic centimeter shall represent one grain of calcium carbonate per U. S. gallon of water when 500 Cc. is titrated by the acid and lacmoid indicator.

One grain = .0648 gram, and one gallon = 3785 Cc.; hence .0648 : 3785 : : X : 500. X = .00856 gram, the corresponding weight of $CaCO_3$ in 500 Cc.

Also, $CaCO_3$ (100.1) : H_2SO_4 (98.086) : : .00856 : y. y = .00839, the weight in grams of H_2SO_4 in one Cc. of the proposed standard solution.

One liter of the standard solution contains $1000 \times .00839 = 8.390$ grams. Hence 8.390 : 49.048 : : s : 1000. s = 171 Cc., the volume of normal sulfuric acid containing 8.390 grams of H_2SO_4. Therefore, if 171 Cc. of normal sulfuric acid be diluted to one liter each cubic centimeter will represent one grain of calcium carbonate as above.

Residual titration. A weight of 1.121 grams of impure zinc oxide was treated with 50 Cc. of hydrochloric acid, one Cc. containing .0337 grams of HCl, and after solution, the excess of acid was titrated by potassium hydrate, requiring 23.4 Cc., one Cc. containing .0498 grams of KOH. What is the percentage of zinc oxide in the sample?

50.0 Cc. of the acid contains $50.0 \times .0337 = 1.6850$ grams of HCl.

23.4 Cc. of the alkali contains $23.4 \times .0498 = 1.1653$ grams of KOH.

Consider the 1.6850 grams of acid divided into two parts, X, the weight neutralized by the zinc oxide, and Y, the weight neutralized by the alkali; then, since one molecule of KOH combines with one molecule of HCl,

56.118 (KOH) : 36.458 (HCl) : : 1.1653 : Y. Y = .7571 grams, and

X = 1.6850 − .7571 = .9279 grams.

Two molecules of hydrochloric acid combine with one molecule of zinc oxide, hence,

72.916 (2HCl) : 81.4 (ZnO) : : .9279 : Z, the weight of the zinc oxide. $Z \times 100 \times 1.121 = 92.42$, the percentage of zinc oxide in the sample; it is assumed that there was no other compound in the mixture capable of neutralizing the acid.

F. Colorimetry. When there are dissolved the weights W of a standard and W' of a sample, containing respectively a and X per cent of a chromogen, and the solutions diluted to an equal depth of color, then measuring respectively V and V' cubic centimeters, the percentage of the chromogen of the sample is found from the formula $X = \frac{a.V'.W}{V.W'}$

G. To calculate the weight of a reagent required for the solution or precipitation of a given body. The equation of the reaction is written, and from the combining weights the proportion is furnished. If, in the equation, a represents the combining weight of the compound to be dissolved or precipitated; b, the combining weight of the reagent; c, the weight of the sample taken for analysis; and x, the necessary weight of the reagent; then $x = \frac{a.c}{b}$

For example, having weighed one gram of impure potassium chromate for analysis, and desiring to know how much crystallized lead acetate to use for precipitating the chromic acid; from the equation —

K_2CrO_4 (194.32) + Pb $(C_2H_3O_2)_2.3aq$ (379.016) = $PbCrO_4 + 2KC_2H_3O_2 + H_2O$,

we see that 379.016 grams of lead acetate precipitate 194.32 grams of potassium chromate. The potassium chromate in the sample cannot exceed one gram, so that the reagent need not be over $\frac{379.016 \times 1}{194.32} = 1.950$ grams or about 20 cubic centimeters of a ten per cent solution.

Some idea can generally be formed as to the proportion of the constituent to be precipitated and the precipitant reduced accordingly, always allowing a slight excess.

H. Gasometry. The volume of a gas or mixture of gases is a function of its temperature and the pressure upon it, and usually is measured at the temperature and pressure of the surrounding air at the time of reading, and saturated with the vapor of water. It has been agreed, however, that all results of gas analysis shall be expressed in volumes of dry gas at a temperature of zero Cent. under a pressure of 760 Mm. of mercury. The conversion is made as follows:

1. Aqueous vapor exerts a pressure or tension varying directly, though not uniformly, with the temperature. At zero it equals that of 4.5 Mm. of mercury, and at 40°, 54.9 Mm. A table for each intermediate degree is given under Tables, *post*.

2. The volume of a gas is in inverse ratio to the pressure upon it — that is, the volume times the barometric pressure divided by 760 gives the volume at 760 Mm. of mercury.

3. A gas expands from zero 1-273rd or .00367 of its volume for each degree Cent. of a rise in temperature, so that the volume as read multiplied by 273 and the product divided by $273 + t°$ (the observed temperature) gives the volume at zero.

Hence the rules —

1. From the observed barometric pressure, less the difference in height, if any, between the mercury in the trough and measuring tube, deduct the tension of aqueous vapor at the observed temperature.

2. Multiply the remainder by the observed volume of the gas and divide the product by 760. The quotient is the volume of dry gas at a pressure of 760 Mm. of mercury at $t°$.

3. Multiply the quotient by 273, and divide the product by $273 + t$. The quotient is the volume of dry gas at 760 Mm. and zero.

Shortly, if V is the volume and d the density of a gas at $t°$ and b Mm. pressure, then the volume V' and the density d' at zero and 760 Mm.—

$$V' = \frac{V}{1 + .00367\,t} \cdot \frac{b}{760}, \text{ and } d' = d\,(1.00367\,t)\,\frac{760}{b}$$

Tables for $1.00367\,t$ when t is between 2° to 40° Cent., and for $\frac{b}{760}$ when b is between 10 and 840 Mm. may be found in works on gas analysis.*

Having the analysis of a mixed gas expressed in volumes per hundred, to change to percentage by weight.

Multiply the percentage of each constituent by the weight of one cubic centimeter of the gas under standard conditions of temperature and pressure. Divide each product by their sum, and multiply the quotient by 100.

Thus,

	Percentage by volume.		Percentage by weight.
Carbon monoxide	52.23 × .001251	= .06534 × 100 ÷ .13767	= 47.46
Carbon dioxide	17.10 × .001977	= .03381 × 100 ÷ .13767	= 24.56
Nitrogen	30.67 × .001256	= .03852 × 100 ÷ .13767	= 27.98

The change from weight to volume is made by a similar calculation.

I. The specific gravity of a mixture of two bodies which coalesce without inter-reaction varies directly with their proportions and serves to determine the percentage of each, the more accurately the greater the difference between their respective densities. If it be known that any two mix without change in volume, in other words, that the curve whose ordinates represent units or decimals of specific gravity, and abscissae the relative percentages in the mixture, is a straight line, the gravity of the mixture is expressed by the equation $D = \frac{V'D' + V''D''}{V' + V''}$ where V' and V'' are the respective volumes of the components; D' and D'', their respective densities; and D, the density of the mixture. Conversely, when the gravity of the mixture and the densities of the components are known, the volumes composing the mixture are

$$V' = V''\,\frac{D - D''}{D' - D} \text{ and } V'' = V'\,\frac{D' - D}{D - D''}.$$

And the weight of one component is found by the formula

$W' = D'\,\frac{AD'' - (BD'' + A)}{D'' - D'}$, A being the weight of the mixture in air, and B, the weight in water (applied, *e.g.*, to mixtures of minerals, as for gold in quartz, galena in calcite, etc.).

For aqueous solutions of metallic salts a specific formula may be deduced from the general one $D = 1 + ap + bp^2 - cp^3$; for example one for potassium chloride $D = 1 + .006217p + .00003574p^2 - 00000018p^3$, in which p is the percentage of the salt in solution, and a, b, and c are empirical coefficients determined by experiment.

Formulae for the calculation of specific gravity by different methods are given below. The principles will be readily understood by bearing in mind that specific gravity is the ratio of the weight of a body to that of an equal volume of water or other standard taken as unity, and that a solid immersed in a liquid loses the weight of an equal volume of the liquid.

* Biedermann's Chemiker Kalander, 15.

SOLIDS.

A solid insoluble in water and of greater gravity. Specific gravity $= G$.
Weight of the solid in air $= A$.
Weight of the solid in water $= B$.

$$\frac{A}{A-B} = G.$$

By Nicholson's aerometer.
Weight to be added to upper pan to sink hydrometer to the mark $= A$.
Substance in the upper pan, the weight in upper pan $= B$.
Substance in lower pan, the weight in upper pan $= C$.

$$\frac{A-B}{C-B} = G.$$

By the specific gravity bottle or Hogarth's flask, etc.
Weight of substance in air $= A$.
Weight of flask and water $= B$.
Weight of flask, substance and water $= C$.

$$\frac{A}{A+B-C} = G.$$

A solid insoluble in water but lighter.
Weigh a heavier piece of metal in water, attach to the solid and weigh both in water.
Weight of the substance in air $= A$.
Weight of the substance and metal in water $= B$.
Weight of the metal in water $= C$.

$$\frac{A}{A-B+C} = G.$$

A solid heavier or lighter than water, but soluble therein. Select another fluid of known specific gravity, lighter than the solid and having no solvent action upon it; *e. g.* an oil.
Weight of the solid in air $= A$.
Weight of the solid in oil $= B$.
Specific gravity of water $= 1$.
Specific gravity of oil $= S$.

$$\frac{AS}{A-B} = G.$$

LIQUIDS.

By the specific gravity flask.
Weight of flask alone $= A$.
Weight of flask and water $= B$.
Weight of flask and the liquid $= C$.

$$\frac{C-A}{B-A} = G.$$

By weighing a solid in water and the liquid
Weight of the solid in the air $= A$.
Weight of the solid in water $= B$.
Weight of the solid in the liquid $= C$.

$$\frac{C-A}{B-A} = G.$$

GASES. (AIR = 1.)

Weight of globe filled with dry air $= A$.
Weight of vacuous globe $= B$.
Weight of globe filled with dry gas $= C$.

$\frac{C-B}{A-B}$ = density of dry gas at t° Cent. and b Mm. barometer.

$\frac{C-B}{A-B} \times \frac{1 + .003665\ t}{V \times .0012934} \times \frac{760}{b}$ = density at zero and 760 Mm. barometer.

To dilute a volume V of a solution of a specific gravity S to a specific gravity S'; the volume of water to be added to V is v, and

$$v = V\frac{S-S'}{S'-1}$$

To convert the specific gravity S of a substance at T° Cent. against water at T°, to gravity S' at t° against water at t'°. Let C be the coefficient of expansion of the substance for one degree; V, the volume of one gram of water at T°; and V', the volume at t'°;

then $S' = \frac{V'\ S.}{V + V(t-T)\ C}$.

In an aqueous solution of a volatile liquid and non-volatile matter (as a solution of alcohol and extractive), the volume of the former may be determined from the difference in specific gravity before and after its removal by evaporation. A measured volume V of the solution of the specific gravity G is boiled until the volatile body is expelled, the solution cooled and made up to the original volume V with water, and the specific gravity G' again observed. If

the gravity of the volatile body is G'', then its proportion by volume v in the original mixture is $v = \frac{V(G - G')}{G'' - I}$. This formula is applicable only where no contraction occurs on mixing the volatile liquid with the solution, otherwise a correction must be applied since the volume of water added after boiling will be less than the volume of the volatile liquid.

Densimetric methods. In these a precipitate is weighed while in suspension in water or a solution. Obviously when a precipitate is introduced into a given fixed volume of water or a solution, the weight of the latter is increased by the weight of the precipitate and diminished by the weight of a volume of water or the solution equal to the volume of the precipitate. Let x be the weight of the precipitate; a, the specific gravity of the dry precipitate; b, the specific gravity of the solution at $t°$, the temperature of the experiment; c, the volume held by the picnometer at $t°$; d, the weight of the volume c of the solution with the precipitate in suspension; then

$$d = b\left(c - \frac{x}{a}\right) + x, \text{ whence } x = \frac{a\,(d - bc)}{a - b}$$

Where a precipitate is formed in a liquid and a portion of the latter withdrawn for further analysis, the ratio of the part to the total liquid can be found as follows. Let the total weight of the liquid, precipitate and flask containing them be A; after drawing off a part of the clear liquid, the total weight of the remaining liquid, precipitate and flask be B: the remaining liquid is filtered, the precipitate washed, ignited and weighed, its weight being C; and the weight of the flask alone is D. Then the weight of the whole of the clear liquid is $A - (C + D)$, and the weight of the portion withdrawn is $A - B$. Hence the ratio of the liquid withdrawn to the whole liquid is $\frac{A - B}{A - (C + D)}$. This formula is only correct where nothing is dissolved from the precipitate on washing with water.

J. In technical analysis, especially organic, there are many mixtures that cannot be separated by any of the known methods, or but imperfectly, yet by computations from data obtained by various transmutations and the determination of constants under different conditions, the proportions of the constituents may be arrived at with a greater or less degree of accuracy. It would occupy too much space to detail any number of examples, but the following will indicate the general trend of schemes of this kind.

The first is the method of Mebus for mixtures of sodium (or potassium) carbonate and bicarbonate.

Two equal weights, A and B, of the sample are dissolved in cold water. A is titrated by normal acid and methyl orange for the total alkali, requiring a Cc. of acid. To B is added normal sodium hydrate (perfectly free from carbon dioxide and baryta) in quantity b Ccs. exactly equivalent to a Cc. of the acid, and also an excess of neutral barium chloride. The precipitated barium carbonate is filtered off, and the filtrate titrated by normal acid, requiring c Cc. From these volumes are calculated the relative proportions of monocarbonate and bicarbonate in the mixture.

To more readily understand the reactions and calculation let us consider what c would amount to

1. Were the sample entirely sodium monocarbonate. Here, since 2NaOH is equivalent to 2HCl, the reactions would be

A. $Na_2CO_3 + 2HCl\ (a) = 2NaCl + H_2CO_3$; and

B. $Na_2CO_3 + 2NaOH\ (b) + BaCl_2 = 2NaCl + BaCO_3 + 2NaOH\ (b)$, and c would be exactly equal to a.

2. Were the sample entirely sodium bicarbonate. Here the reactions would be

A. $Na_2CO_3.H_2CO_3 + 2HCl\ (a) = 2NaCl + 2H_2CO_3$, and

B. The caustic alkali abstracts one-half of the CO_3 from the bicarbonate —

$Na_2CO_3.H_2CO_3 + 2NaOH = 2Na_2CO_3 + 2H_2O$; and with barium chloride,

$2Na_2CO_3 + 2BaCl_2 = 4NaCl + 2BaCO_3$.

The filtrate is exactly neutral and c is zero.

3. Hence 100 per cent of monocarbonate is shown when c equals a, and 100 per cent of bicarbonate when c equals zero. The difference between a and c in a determination is a volume of normal acid equal to the volume of normal sodium hydrate reacting with the bicarbonate. This volume in cubic centimeters times .040058 (the weight of sodium hydrate in one cubic centimeter of the normal solution) is the weight d of sodium hydrate reacting; and since $Na_2CO_3.H_2CO_3\ (168.116) + 2NaOH\ (80.116) = 2Na_2CO_3 + 2H_2O$, from the proportion 168.116 : 80.116 : : X : d may be calculated X, the weight of sodium bicarbonate in the sample.

For the analysis of crude soda-lyes that contain sodium carbonate, hydrate, sulfide, sulfite and thiosulfate, a volumetric method is due to Kalmann and Spueller.* The method is based on the insolubility of barium sulfite and solubility of the thiosulfate, and precipitation of a sulfide by zinc in alkaline solutions.

Five equal volumes of the liquid are measured and titrated as follows by normal acid and decinormal iodine solutions.

A. By acid and methyl orange, neutralizing the *carbonate, sulfide, hydrate* and *one-half* of the *sulfite* (sodium bisulfite is neutral to methyl orange).

B. By iodine, reacting with the *sulfide, sulfite,* and *thiosulfate.*

C. The sulfide is precipitated by a zinc salt, the zinc sulfide filtered off, and the filtrate acidified and titrated by iodine; there are oxidized the *sulfite* and *thiosulfate.*

D. The sulfite is precipitated by barium chloride, and the filtrate titrated by acid; there are neutralized the *hydrate* and *sulfide.*

E. The sulfite is precipitated by barium chloride, the solution filtered, and the filtrate acidified and titrated by iodine; there are oxidized the *sulfide* and *thiosulfate.*

Combining the above data we obtain the volumes of the acid and iodine solutions corresponding to the following: —

B. $Na_2S + Na_2SO_3 + Na_2S_2O_3$ *E.* $Na_2S + Na_2S_2O_3$	..... *F.*	The difference is iodine solution equivalent to the Na_2SO_3.
B. $Na_2S + Na_2SO_3 + Na_2S_2O_3$ *C.* $Na_2SO_3 + Na_2S_2O_3$	..... *G.*	The difference is iodine solution equivalent to the Na_2S.
E. $Na_2S + Na_2S_2O_3$ *G.* Na_2S	..... *H.*	The difference is iodine solution equivalent to the $Na_2S_2O_3$.
D. $Na_2S + NaOH$ $\frac{G}{10}$. Na_2S	..... *I.*	The difference is acid solution equivalent to the NaOH.
A. $Na_2CO_3 + Na_2S + NaOH + \frac{1}{2} Na_2SO_3$ $D + \frac{F}{20}$. $Na_2S + NaOH + \frac{1}{2} Na_2SO_3$	..... *J.*	The difference is acid solution equivalent to the Na_2CO_3.

In computing *I* only one-tenth of *G* is subtracted from *D* since the iodine solution is *decinormal* while the acid solution is *normal;* similarly in computing *J*, one-tenth of one-half of *F* is subtracted.

Given a mixture containing the three sugars, sucrose, dextrose, and levulose; an aqueous solution is clarified and diluted to a definite volume, and three aliquot parts, A, B, and C are withdrawn. Each part is boiled with Fehling's solution (*vide* Sugar), producing a precipitate of cuprous oxide, as follows —

A. Directly. The precipitate is *a* grams of cuprous oxide from the reaction with the dextrose and levulose, sucrose having no action on Fehling's solution.

B. After conversion of the sucrose into equal parts of dextrose and levulose by inversion by a dilute acid; the precipitate is *b* grams of cuprous oxide coming from the reaction with the original dextrose and levulose, and the dextrose and levulose from the sucrose.

C. After destruction of the levulose by heating with concentrated hydrochloric acid;

* Dingl. Polyt. Journ. 264—456.

this also inverts the sucrose and destroys the levulose formed. There is precipitated c grams of cuprous oxide from the reaction with the original dextrose and the dextrose from the sucrose.

Calling the weight of the original dextrose D and levulose L, and the dextrose from the sucrose D' and the levulose L'; then the weight of the precipitate

From $D + L = a$

" $D + L + D' + L' = b$

" $D + D' = c$

" $D' + L' = 2D' = b - a$

" $L + L' = b - c$

" $D' = \frac{1}{2}(b-a)$

" $D = c - \frac{1}{2}(b-a)$.

" $L = a - [c - \frac{1}{2}(b-a)]$

Now, one gram of cuprous oxide results from the reaction with either .260 gram dextrose, .253 gram levulose, or .262 gram inverted sucrose; and one gram of inverted sucrose results from the inversion of .950 gram sucrose; hence

$$(b-a) \times \frac{.95}{.262} = \text{weight of sucrose in the mixture.}$$

$$[c - \frac{1}{2}(b-a) \times \frac{1}{.260} = \text{weight of dextrose in the mixture.}$$

$$(a - [c - (b-a)]) \times \frac{1}{.253} = \text{weight of levulose in the mixture.}$$

A number of organic and inorganic compounds are quantitatively oxidized by potassium permanganate in an alkaline solution, the permanganate breaking up in this way — $K_2O + 2MnO_2 + 3O$, the binoxide of manganese precipitating as a fine hydrated powder, and the three atoms of oxygen acting to oxidize the organic compound.

A determination by this reaction may be done by (1) filtering off the manganese binoxide and determining its weight by a gravimetric or volumetric process; or (2), having used a known volume of standard permanganate solution for the operation, to filter through asbestos and determine the unreduced permanganate in the filtrate by a volumetric titration. In either case the weight of the organic compound is learned by a simple calculation.

A more expeditious plan is (3) to employ a known volume, a moderate excess, of standard permanganate for the determination, then, without filtering, to run in a known volume, an excess, of a standard reducing solution, this reducing both the excess of permanganate and the precipitated manganese binoxide; finally the excess of the reducing solution is determined by titration by standard permanganate.

The calculation for the last named process can be made in several ways of which two are given below. Taking sodium thiosulfate as an example, the reaction between it and potassium permanganate is expressed by the equation —

(1). $6Na_2S_2O_3.5aq + 8K_2O.(MnO)_2.O_5 + 2H_2O = 16MnO_2 + 6Na_2SO_4 + 6K_2SO_4 + 4KOH + 5aq.$

Of the 40 atoms of available oxygen of the permanganate, 16 go to form MnO_2 and 24 to oxidize the thiosulfate.

On now adding sulfuric acid and an excess of a standard solution of ferrous sulfate to the turbid liquid, first the excess of the permanganate is reduced —

(2). $10FeSO_4 + K_2O.(MnO)_2.O_5 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$

then the manganese binoxide is dissolved —

(3). $2FeSO_4 + MnO_2 + 2H_2SO_4 = Fe_2(SO_4)_3 + MnSO_4 + 2H_2O.$

Finally the excess of ferrous sulfate is titrated by standard permanganate of the same strength as originally used, as per equation (2) above.

A. Calling the original volume of permanganate solution c, and the volume used in the final titration d, then the total volume used is $c + d$ cubic centimeters.

Now this volume $c + d$ contains a certain weight of potassium permanganate and this a certain proportion of available oxygen. The available oxygen we may consider as divided into two parts; one part goes to oxidize the ferrous sulfate to ferric sulfate, the other to oxidize the thiosulfate as in equation (1) above. This will be evident when the rationale of the process is considered. On mixing the permanganate and thiosulfate solutions, the oxygen of the original volume of permanganate divides into three parts; the first part (A) oxidizes the thiosulfate to sulfate; the second part (B) unites with

MnO to form MnO_2; the third (C), that of the excess of permanganate, remains unseparated. Now, on adding the ferrous solution, the oxygen of (B) plus (C) plus that of the permanganate used in the titration react with the iron to exactly convert it to ferric sulfate.

We have therefore to calculate the available oxygen in the total permanganate and subtract from it the part required to oxidize the ferrous sulfate; the remainder is the oxygen taken up by the thiosulfate, from which the weight of the latter can be calculated.

1. From equation (2) we see that ten atoms of iron react with five atoms of oxygen; that is, in the ratio of 10×56 to 5×16, or as 7 to 1. Hence $\frac{1}{7}$ of the weight a of iron oxidized by one cubic centimeter of the permanganate solution gives the weight of available oxygen in one cubic centimeter of the permanganate solution. And the total volume of permanganate solution used contains $\frac{1}{7} .a .(c + d)$ grams of available oxygen.

2. Now, if in the volume of ferrous solution added there are b grams of iron, then $\frac{1}{7} .b$ will be the weight of available oxygen of the permanganate required to oxidize the iron.

3. Therefore $\frac{1}{7} .a .(c + d) - \frac{1}{7} .b =$ the weight of oxygen reacting with the thiosulfate.

4. From equation (1) we learn that six molecules of thiosulfate ($6 \times 248.32 = 1489.92$) react with 24 atoms of oxygen of the permanganate ($24 \times 16 = 384$). Hence one gram of oxygen corresponds to $\frac{1489.92}{384}$ grams of thiosulfate.

5. Finally, $\left(\frac{1}{7} .a .(c + d) - \frac{1}{7} .b\right) \times \frac{1489.92}{384} = X =$ the weight of crystallized sodium thiosulfate in the material analyzed. This may be reduced to $X = .5543\ (a.c + a.d - b)$.

B. A somewhat similar calculation is as follows. It is based on the principles that certain proportional weights of oxygen are required to oxidize respectively one gram of thiosulfate to sodium sulfate (in an acid solution), and one gram of iron from ferrous sulfate to ferric sulfate, the proportions shown by the equations —

$$4K_2Mn_2O_8 + 5Na_2S_2O_3.5aq + 7H_2SO_4 = 5Na_2SO_4 + 4K_2SO_4 + 8MnSO_4 + 7H_2O; \text{ and}$$
$$4K_2Mn_2O_8 + 40FeSO_4 + 32H_2SO_4 = 20Fe_2(SO_4)_3 + 4K_2SO_4 + 8MnSO_4 + 32H_2O.$$

From these equations it is seen that four molecules of permanganate oxidize respectively five molecules of thiosulfate and 40 atoms of iron. Hence one cubic centimeter of permanganate solution will oxidize iron and thiosulfate in the ratio of 40×56 to 5×248.32; or, if one cubic centimeter of permanganate solution oxidizes a grams of iron, it will oxidize $a \times \frac{5 \times 248.32}{40 \times 56}$ grams of thiosulfate.

If e cubic centimeters of permanganate solution oxidizes the volume of ferrous solution added, and $c + d$ is the total volume of permanganate solution used, then $c + d - e$ is the volume of permanganate solution oxidizing the thiosulfate.

Hence $a \times \frac{5 \times 248.32}{40 \times 56} \times (c + d - e) = X =$ the weight of crystallized thiosulfate. More conveniently expressed, $X = .5543\ .a.(c + d - e)$.

CHAPTER 9.

ERRORS AND PRECAUTIONS.

On finishing the calculation of an analysis there may arise two questions: how nearly should the results agree with those deduced from the formula, or otherwise ascertained, to be considered satisfactory? and to what cause should a failure, manifest or inferential, be attributed?

It is plain that, as a general proposition, the first question admits of no answer; for although depending primarily on the intrinsic accuracy of the method employed, yet the correctness of every determination is contingent to a great extent on the skill of the analyst, the care and attention given at the various stages of the analysis, and other conditions. So that no general rule can be laid down, even approximately. As to the methods themselves, the most accurate are capable, when prosecuted with the utmost care in every respect, of affording results within a variation of not over one-tenth of one per cent, grading down to those where an inaccuracy as high as five or ten per cent is not uncommon.

Perhaps the best criterion is to be found in the test-analyses appended to the original description of the methods (which should always be consulted when possible), however to be accepted at times with some allowance for the natural inclination of the deviser to excuse and suppress the more unfavorable results.

And to the second query only a like indefinite reply can be made. Assuming that the method of analysis followed is unimpeachable, one should first repeat the calculations; then examine each precipitate (always to be preserved until the entire analysis is finished) to learn whether it is of the assumed composition and for impurities from foreign sources or in the form of other constituents of the sample that have been imperfectly separated; then the strength and purity of the reagents used; and lastly the substance analyzed in respect to purity and freedom from moisture. If none of the above is found defective, the analyst is forced to the conclusion that faulty manipulation at some stage has been responsible, and his only recourse is a repetition of the entire analysis.

Outside of defects in the method itself, the errors most likely to be incurred in the course of an analysis may be recounted as follows:

1. A defect in the sample. Although directions for sampling and the preparation of the sample are not commonly included in the brief of a method, yet the importance of properly conducting these operations cannot be too much emphasized. Discrepancies in analyses of one material that are due solely to an imperfect sample are frequently charged to the remissness of the chemist or a faulty method. Within the observation of the author, the great majority of the variances among chemists have arisen from ignorance or carelessness in this respect.

In general, the irregular distribution of the various constituents in animal and vegetable matter and heterogeneous materials both natural and artificial, and the effects of imperfect mixing, liquation and segregation in manufactured products demand the greatest care in the selection of what is to be a

representative sample. Personal supervision of the operation of sampling by the chemist himself is always desirable.

In the analysis of a complex powder it must be seen to that the particles are well intermixed before weighing out the portion for analysis, and that the heavier particles have not sifted to the bottom of the bottle. It is a good plan to mix a powder by rolling it to and fro on a paper, then flatten the pile to a thin layer and gather a little here and there until enough is collected for the analysis.

The expediency of grinding an ore or mineral to a *uniformly* fine powder, whether it is to be resolved by an acid or fluxed, will soon be learned by experience, the rapidity and completeness of the subsequent decomposition well repaying the labor of a thorough trituration. Illustrations are found in certain native silicates of which the silica separates and gelatinizes at once on treatment with hydrochloric acid, and coarse particles are inclosed by the silica and protected from further action of the acid; similarly alloys containing tin, on treatment with nitric acid the metastannic acid left insoluble retains less of the other metals in proportion as the alloy was finely divided.

It must not be overlooked, however, that grinding changes the amount of moisture in a sample to a greater or less extent, and that oxidation may occur even in apparently stable inorganic compounds — Craig* has remarked that a noticeable oxidation attends the grinding of pyrite in an agate mortar.

The chemist may receive for analysis a solid that has become superficially altered in some way (as a bar of soap containing much less water at the surface than within), and in taking from it a portion for the analysis, a question may arise as to the propriety of including or rejecting the parts that have suffered alteration. Or a sample may be received containing matters of such a nature that a doubt may be entertained as to whether they formed an integral part of the original or were accidentally included during the collection or transportation of the sample. A decision in matters of this kind must be left to the judgment of the chemist.

It is always advisable to analyze an unstable organic mixture for solution as early after receipt as possible. Alterations in composition, induced by exposure to air and moisture, bacilli and ferments, the escape of gases, absorption by containers, etc., may cause a considerable difference in the results of analyses made at intervals more or less protracted. The same is true, though to a less extent, of course, of certain inorganic mixtures.† If it is impracticable to begin the analysis at once, a preservative may perhaps be compounded with the sample, of a nature and in a quantity that will not interfere with the subsequent analysis. The age, mode of preservation, material of the container and protection afforded, any evidences of an attempt at tampering, etc., and the general condition of the sample should be recorded on receipt for future reference.

In the preparation for analysis of chemical compounds one should guard particularly against mother-liquor inclosed in cavities of crystals, oxidation from exposure to the air, and adhering moisture; and the partial dissociation of double salts on crystallization is more common than is generally supposed.

2. Imperfect weighing and measuring. If the analytical balance is used by more than one operator its equilibrium and general condition must be seen to before each weighing. The weights should be tested from time to time, the intervals depending on the frequency of their use and the care given to their preservation.

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* Journ. Anal. Appl. Chem. 1892—45.

† Wiley, Agricultural Anal. 2—84.

All weighings of glass or metal containers are only to be regarded as final after a sufficient time has elapsed for them to acquire the temperature of the balance-case. According to Miller,* on wiping a small flask with a linen cloth in very dry weather, an electric charge was generated which required .080 gram in the opposite pan to restore equilibrium, the charge requiring considerable time for entire dissipation.

A correction is to be made in the most accurate weighings for the buoyancy of the air (page 89); for solids and liquids the loss is too small to be considered in general work, though for gases it cannot be neglected.

The weight of a material best suited for the determination of a constituent is fixed by several conditions. The general rule holds that the greater the weight the less is the result changed by the constant unavoidable errors of analysis. Exceptions where the use of large amounts are restrained, are some solutions containing a constituent that is slowly decomposed at the heat of evaporation, and consequently the evaporation must be conducted both with expedition and at a low temperature. Similarly, a liquid that leaves a residue on evaporation that consists mainly of organic matter with a small proportion of inorganic salts; on subsequently burning off the carbon of a large residue the heat of combustion may rise so high as to fuse or volatilize the inorganic matter. These objections may be overcome of course by providing dishes and crucibles of a suitable shape and adequate size.

The exactness to which a residue or precipitate should be weighed depends largely on the intrinsic accuracy of the method, the skill and care with which the analysis is prosecuted, and, other things being equal, the weight of substance taken for analysis. In general, it is unnecessary to weigh closer than one milligram. There are a few exceptions, *e. g.*, in the fire assay of gold ores where the gold button must be weighed with the greatest accuracy; on the other hand, for the ordinary run of gold ores, taking as high as thirty grams for the crucible assay, an error of a few centigrams of the weight of the ore has no practical significance.

In duplicate or triplicate determinations it is advisable that the portions of substance weighed for a determination should differ somewhat in weight as the effect of a constant error in the analysis is more easily detected than if the weights were identical.

The space occupied by a precipitate or insoluble residue of moderate bulk in a solution of definite volume is often negligible in ordinary analyses, for many apparently voluminous precipitates are so attenuated that they really displace but little of the liquid; if the bulk is considerable, however, a correction must be made.

In volumetric analysis the error ordinarily incurred in measuring a liquid is undoubtedly greater than in weighing the substance, but as it is not with the liquid itself that we are concerned but the reagent dissolved therein, it is plain that the effect of errors in measurement can be reduced indefinitely by decreasing the ratio of the reagent to the volume of water holding it in solution — in other words, the more dilute the solution the less care need be taken in measuring it. On the other hand the more dilute the solution the greater the volume needed to bring out the end reaction of a titration distinctly, so that there is no real advantage in weakening a titrand beyond the point where this will be sharply defined by a single drop.

In the measurement of a gas it must be assured that it is either perfectly dry or saturated with moisture. After standing for a time over water or a dilute aqueous solution saturation may be assumed, but not if the liquid is hygro-

* Journ. Amer. Chem. Socy. 1898—428.

scopic, such as a strong solution of an alkali, concentrated sulfuric acid, etc.

3. Mechanical losses and gains. Despite more than ordinary care there may often happen a loss in transferring a liquid from one vessel to another, in boiling or distilling, igniting a precipitate, etc., or a gain from ubiquitous dust or the vessels used in evaporations. It must be left to the discretion of the operator whether a mishap of this kind is of sufficient consequence to constrain the discontinuance of the analysis. Where it is reasonably certain that the amount lost is so small a proportion of the original as not to reduce the weight of the predominating constituent appreciably, it is of course not imperative that the analysis be terminated summarily, for "here as elsewhere, in experimental science, the golden rule is neither to strain at the gnat nor to swallow the camel." However, the student should strive to attain such a mastery over the manipulations that even a comparatively unimportant loss will be of rare occurrence.

Transferring a solid, liquid or gas from one container to another is frequently attended by loss, and can often be avoided by choosing a vessel of the proper size or shape at the beginning. As the loss of a part of a dilute solution is of less consequence than the same amount of one more concentrated, it is advisable to dilute a strong solution before this operation provided there is no reason to the contrary.

Some salts have a tendency to crystallize above the surface of a solution as it evaporates; the liquid by diffusion through the crust extends until eventually it creeps over the edge of the dish or crucible down the outside. A preventative is slightly greasing the edge with oil or vaselin; or by applying the heat above the surface of the liquid.

The effervescence from the escape of a gas when a metal, sulfide or carbonate is dissolved in an acid may easily cause a loss of fluid by projection unless the containing vessel is capacious and covered. An Erlenmeyer flask is suitable, or an evaporating dish in which stands inverted a wide-stemmed funnel of slightly less diameter. Where the reaction is expected to begin suddenly, accompanied by violent boiling up, the sample should be dropped into the acid in several small portions. This direction applies particularly to metals and nitric acid; and has also the advantage in this case that the metal comes in contact with strong acid only, lessening the danger of any associated element (as sulfur) escaping oxidation as might happen were the acid added in portions to the metal. Yet unless some special oxidizing or other action is desired, the acid should be so dilute that solution proceeds slowly and quietly.

Or as the solution nears the point of saturation a tenacious film of crystals may cover the surface followed by a vigorous spattering as bubbles of steam perforate it; so a constant stirring or rocking of the vessel must be kept up until solidification. Salts of ammonia are especially troublesome in this way.

Viscous organic bodies containing water invariably froth in the retort and some of the foam is liable to pass over it into the receiver. This may be prevented by "dead-melting" — maintaining the liquid in the molten state for some time, then decanting from the water deposited.

In condensing a distillate an uninterrupted stream of cold water must be kept running through the condenser, and the latter should expose an ample surface to the vapor; and be made of thin glass, or preferably of metal (a better conductor of heat) for distillates containing no free acid.

The complete absorption of a gas in a liquid may be insured by passing it slowly through several absorption bulbs, the number depending on the solubility-coefficient of the gas. One bulb may answer when a marked chemical action ensues between the gas and absorbent.

In distillations, organic combustions, etc., the gas tightness of the rubber or ground-glass connections, stoppers, and insealed wires must be assured before the determination is begun, best by attaching a small manometer and compressing the air within the apparatus. Should the manometer indicate a leak, the location may be found by wetting suspected places with soap solution, when a chain of fine bubbles will appear whenever air escapes. Smearing with glycerin, syrupy phosphoric acid, or a mixture of rubber and beeswax * will tighten a loose fitting joint, though it is not the best policy to permit a makeshift of this kind in an important analysis.

In the combustion of an organic body a blank determination should precede the actual analysis. Usually a slight fairly constant increase will be found in the calcium chloride and potash bulbs, but it should not be great enough to vitiate the results of a test.

A liquid has often to be clarified without increasing its volume, and here the filter is not moistened previous to filtration. It is said† that from adsorption, the first few drops of the filtrate hold less in solution than the original, and these should be rejected if the fraction first filtered is to be a representative of the concentration of the entire filtrate. Contributing to the dilution is the hygroscopic moisture of the paper.

4. Imperfect solution. Continuous percolation alone will readily and thoroughly extract a soluble constituent from a substance of an open and porous character, not inclined to swell or gelatinize during the operation, otherwise may fail even when the percolation is greatly prolonged, for the reason that the usual construction of the apparatus does not provide a convenient way of stirring up the substance at intervals, and therefore the solvent, following the paths of least resistance, will avoid the less permeable aggregations. It is safer in most cases to precede the extraction by a digestion in a beaker.

A percolation is usually considered complete when the drops fall uncolored, but when the principle to be extracted is colorless it may have passed entirely into solution long before the coloring matter. The percolate should be tested from time to time in the same way as the washings from a filtration. At the beginning the percolate may run cloudy and is to be returned to the percolator, but care must be taken against mechanical loss since the first fraction is so comparatively rich in extractive.

The solvent employed for the extraction of a principle from a mixture should contain no fixed impurities, and should also be free from any other solvent, whose presence might cause small amounts of other principles to enter the solution. Commercial ether usually contains water and alcohol and must be purified before using, while most other solvents are found on the market sufficiently pure as a rule for immediate use.

In the lixiviation of one constituent of a mixture it must be remembered that the other constituents are brought in contact not only with the pure solvent but also with a more or less concentrated solution of the soluble constituent, toward which their deportment may be quite different. Similarly, undried vegetable matter may contain so much moisture that when percolated by strong alcohol, the first portion of the percolate contains also whatever else is soluble in weak alcohol, this precipitated in part by the stronger spirit that follows.

5. Losses and gains on evaporation and ignition. The haloid salts of a few metals are volatilized to some extent when their solutions are boiled, while many acids and organic solutions cannot be evaporated without extensive loss or decomposition. If concentration by heat is unavoidable, the combination

* Journ. Amer. Chem. Socy. 1898—678.

† Ostwald-McGowan, Foundations of Anal. Chem. 22.

may be previously changed to one not volatile, or the vapor condensed or absorbed.

With easily decomposed organic solutes, either a temperature below the boiling point is employed, or the liquid is allowed to evaporate spontaneously. For an organic solvent of low boiling point, a temperature of 30° to 40° is better, as spontaneous evaporation so far cools the liquid that moisture from the air is condensed and absorbed. And in an evaporation or distillation the possibility of a liquid being carried off in the vapor of one having a lower boiling point should not be overlooked.

Precipitates containing a metal volatile at a red heat or below suffer a certain loss when ignited with carbon. When surrounded by a filter paper, loss cannot be entirely prevented, although its extent is much less than commonly believed. Even ignition for a long time in a platinum crucible over a Bunsen burner may have the same effect through permeation of reducing gases. By removing as much as possible of the precipitate from the paper, moistening the latter with solution of ammonium nitrate, and burning at the lowest heat, the loss will not be serious, as a rule. A Gooch crucible is most suitable for precipitates of this nature.

Refractory forms of carbon can be burned rapidly from associated inorganic matter by turning a gentle stream of oxygen into the crucible. This scheme answers well where the inorganic matter is practically infusible, as silica, magnesia, alumina, but is not advisable for residues that fuse or volatilize at a moderate temperature, since the local heat of combustion is here much above redness.

The temperature of ignition of precipitates may usually vary between wide limits. Exceptions are where a certain constituent element or compound is to be volatilized, and a heat lower than that directed in the method followed will fail to drive it off completely. Conversely, if the integrity of the precipitate is to be preserved too high a heat may fuse it or volatilize some constituent.

The loss through volatilization of a part of a constituent of a precipitate during ignition may be restored by a subsequent process (page 103), but the better plan is to prevent it if possible.

Change of composition through oxidation at a red heat can be avoided by transmitting a current of hydrogen or carbon dioxide into the crucible; this plan is well adapted for the ignition of metallic sulfides that contain or have been mixed with free sulfur, leaving a definite pure sulfide on ignition.

If a precipitate and filter have not been at least partly dried before ignition, a loss by projection may be expected when the heat of a burner is suddenly applied to the crucible. This will not happen, however, after filtration by the vacuum pump, or after the paper has been opened on a porous tile. And although a pulverulent precipitate or residue has been thoroughly dried, if ignited too hastily, the smoke and gases from the paper are apt to carry off traces of the finer particles. Economy of time and security against loss are insured by a close observance of the directions given on page 103.

Corrosion of containing vessels. Experiments by various chemists show plainly that discrepancies in accurate analyses are frequently traceable to the ingredients of glass or porcelain glaze acquired by a solution. The error from this source is evident when a large volume of liquid is evaporated in a large vessel to a small bulk, and the liquid transferred to a smaller tared dish, evaporated to dryness and the residue weighed; here the amount of glass dissolved is frequently several milligrams, and may reach to a centigram or more. And in precipitations, any dissolved silica or calcium silicate is usually enveloped and carried down with the precipitate.

Some authorities state that the glass and porcelain glaze are dissolved in toto, others incline to the belief that the alkalies are extracted disproportionally to the other constituents. It is said that the resistance to corrosion by water or a solution is at a minimum with new vessels, rapidly increasing on continued contact—possibly by the removal of a superficial film structurally modified by contact with the air—and that allowing the vessels to stand filled with water for several days will greatly reduce the amount dissolved during subsequent use.

In most cases, porcelain is less acted on than glass, and platinum than either. According to Bohlig,* 100 cubic centimeters of water dissolved every two seconds from a glass flask enough free alkali to neutralize one cubic centimeter of tenth-normal acid; this glass was, no doubt, of a composition exceptionally soluble.

Platinum is usually attacked to a slight degree by melted fluxes; traces of platinum can often be discovered in a solution of the fusion of a mineral with alkali carbonate.

6. Precipitation. Too great an excess as well as a deficiency of the precipitant must be guarded against, the former by calculating the amount of reagent required, and the latter by testing the first portion of the filtrate.

A slight excess of the precipitant markedly reduces the amount of the precipitate retained in solution. This fact is well illustrated in the titration of silver nitrate by solution of sodium chloride; a mixture of their exact combining weights leaves a clear supernatant liquid in which *either* of the salts produces a slight precipitate of silver chloride by lowering the solvent power of the liquid. As the precipitant is always in slight excess in every precipitation, the correction of the weight of the precipitate by the figures of the published tables of the solubilities of precipitates in water is inapplicable.

Fibres of filter paper, dust and organic matter in general, may impede the complete precipitation of a base by alkalies and some of their salts, or a chemical action may result in the reduction of the per-salt of a sensitive compound to a proto-salt or lower, giving rise to some perplexity. The addition of a few drops of nitric acid or a crystal of potassium chlorate to the hot acid solution will destroy small amounts of organic matter. If a volatile organic compound is present in quantity, it may be expelled by evaporation to a small bulk; if non-volatile, by evaporation to dryness, and gentle ignition to carbonization, or fusion with an oxidizing flux.

When the solution of a reagent contains an adjuvant whose purpose is to prevent the co-precipitation of other bodies, the formation of the precipitate is somewhat retarded as a rule, and that it may not be incomplete or include other bodies a certain ratio must be preserved between the reagent, the adjuvant, and the body to be precipitated.

Many precipitates deposit so slowly that several hours repose is required for their complete segregation. Generally indicated by a clear supernatant liquid, in case of doubt it is well to make sure by setting aside the filtrate for some time.

Unless otherwise ordered for special reasons, a precipitant is always introduced into a solution to be precipitated in the form of a solution, and never as a powder or crystals, as in this case occlusion of the precipitant is highly favored.

The valence of polyvalent metals to be precipitated is always to be ascertained before the precipitant is introduced, since most reactions are limited to

* Zeits. Anal. 28—518.

a particular phase. And generally, attention must be paid to the precautions regarding volume, temperature, reaction, etc., of solutions laid down in the description of the method or left to the discretion of the chemist.

7. Defective separation. The contamination of a precipitate by another formed by some secondary reaction with the oxygen of the air, or fumes of acids, ammonia, hydrogen sulfide, etc., abundant in a laboratory occupied by several workers, can be prevented to some extent by keeping the solutions covered as far as practicable, but it is the better plan to select another method that is not subject to this drawback.

A separation by the evaporation of a solution to dryness, causing one constituent to pass to an insoluble form, is seldom complete after but one evaporation, especially where the solution contains also much saline matter, and the residue should be again taken up with a little water or acid and evaporated. Some advise heating the residue to above 100°, but it is not well to much exceed this temperature on account of possible inter-reactions between the constituents of the residue.

In the extraction of a body by an immiscible solvent (page 77), an emulsion may be formed by too violent shaking in mixing the solvents, the ease of emulsifying the two liquids being dependent on the nature of the aqueous solution and its reaction and that of the organic solvent. To induce the liquids to again separate into layers there may be applied a gentle heat, or the emulsified portion drawn off and shaken with some of the organic solvent, or a little alcohol may be added to the mixture; if none of these expedients is successful, filtration or distillation must be resorted to.

The decomposition of a complex precipitate or residue by a reagent, a part becoming transformed to another insoluble compound and a part entering solution, seldom affords a complete separation, and it is prudent to further test the insoluble matter for inclosed particles of the original.

8. Filtration and washing. The common grades of filter paper may contain a considerable amount of soluble impurities. Padé found in a sample of white filter paper 10.4 per cent of ash of which 7.4 per cent was calcium sulphate; but such a large percentage of ash is very unusual. The quality of the paper sold for quantitative analysis by reputable dealers is generally sufficiently pure for all ordinary analyses.*

The asbestos used in the Gooch crucible must always be previously purified by boiling with hydrochloric acid, and in accurate analyses it is prudent to dissolve out the precipitate after weighing and reweigh the crucible and felt to discover if any notable loss has been sustained during the filtration and washing; but strong acids and caustic solutions are not admissible for this purpose on account of their solvent action on pure asbestos.

In practice the extent to which a precipitate is to be washed is governed by several considerations: (1), the concentration of the solution; (2), the adhesion of the solution to the precipitate; (3), the adsorption of the solution in the precipitate; (4), the adsorption of the solution in the filter paper; (5), irregularities in the permeation of the precipitate by the wash water; and (6), ununiform displacement of the solution by wash water, due to the mixing of the two.

Defective washing of a precipitate is a most frequent source of high results, especially when the subject is flocculent or gelatinous, enveloping impurities and retaining them with some tenacity. The precipitate, if at all bulky, should be well roused during each addition of wash water, and care be taken that the edge of the paper is not neglected. With a precipitate difficult to wash, it is

* Journ. Socy. Chem. Ind. 1898—70.

well, after a preliminary washing, to disintegrate it by drying or freezing, then complete the washing; or to transfer it from the filter back to the beaker by a jet of water from the wash bottle, and boil for a short time. The first way is safer with precipitates that may slightly dissolve on boiling with a solution of the impurities — *e. g.*, traces of an alkali chromate are formed when chromic hydrate is boiled with a solution of an alkali chloride.

On the other hand, too low results may sometimes be attributed to imperfect washing; as where a precipitate on ignition forms a volatile compound with the remaining impurity, *e. g.*, ferric hydrate reacts with ammonium chloride to form ferric chloride.

The last washing should always be tested for proof that everything soluble in the wash water has been extracted. Where the precipitate itself is somewhat soluble a correction may sometimes be applied for the amount passing into solution in the wash water, but no reliance can be placed on the tables of the solubilities of precipitates in water for this purpose, for, among other reasons, the wash water is usually in contact with the precipitate for so short a time that the solution never reaches saturation.

For a final examination as to the purity of a weighed precipitate it may be dissolved or lixiviated by a suitable liquid, lixiviation best after a structural or molecular change has destroyed the absorptive power of the precipitate or rendered it more permeable.

9. Volumetric analysis. Although the graduation of volumetric ware is usually accurate enough for practical purposes, yet the correctness of any instrument should never be taken for granted.* Directions for recalibrating will be found on page 186.

Aqueous solutions, alcohol, and the like adhere to the interior of glass vessels to a greater or less extent than pure water; thus, a pipette calibrated for 1000 grains of water delivered only 995.2 grains of a strong solution of zinc sulfate. In dealing with fairly concentrated solutions, the more accurate plan is that of weighing.

Pipettes and burettes should always be in a vertical position while their contents are discharging; even an inclination of ten degrees perceptibly lessens the volume delivered.

In practice small changes in the temperature of volumetric solutions need hardly be considered, but if differing more than a few degrees from that at the preceding standardization, should be raised or lowered to correspond, or restandardized. Corrections for a change in temperature are open to criticism owing to the specific rate of expansion of solutions even when dilute, and scanty and unconfirmed data therefor.

It has been recommended that stock solutions be made of such a strength that equal or nearly equal volumes shall react "in order that the expansions and contractions which the two liquors undergo, by reason of changes in temperature of the laboratory, should be without influence on the results" of the titration. But this direction holds only when it has been ascertained that the two equivalent solutions expand by heat in the same ratio. However, it is advisable where a stock solution is used from time to time to verify the strength of a standard solution, that the bottles be stored side by side that they may remain at the same temperature.

The temperature of the volumetric room should be fairly constant, for if a solution is warmer or colder than the air of the room, when poured into a narrow burette the solution will gradually contract or expand during a titration.

The depth of color to be considered as the end-point of a titration is to some

* Analyst. 1898—3.

extent a matter of individual choice. Some accept the least indication of a change, while others prefer an unmistakable deep tint, but in either case there should be an endeavor at uniformity in the standardization and the titration of the sample analyzed. A common fault of beginners is that of introducing too great a proportion of indicator to the volume of the titrate, the pronounced color unduly extending the transition tint.

The error due to the excess of titrate required to produce the end reaction is generally negligible. Where otherwise, a correction is to be found by compounding a blank solution of the same volume as the titrate, and of about the same composition, including the products of the reaction. The fraction of a cubic centimeter of the titrand required to plainly show the end-point in the solution is to be deducted from the actual determination and the same correction be made in the standardization.

When the end-point is observed by testing a drop of the titrate, the amount removed for this purpose in the course of a titration undoubtedly occasions a loss. But considering the comparatively great bulk of the titrate and that the drops are mostly withdrawn toward the end of the operation (when the concentration as regards the reacting body has been largely reduced), the deficit is seldom of consequence.

A persistent tenacious froth may be thrown up on stirring certain titrates of an organic nature that intercepts and retains drops of the titrand. The tendency may be diminished by the addition of alcohol — sometimes the vapor of alcohol alone will dissipate the foam.

10. Colorimetry. The depth of color of a liquid increases with the thickness of the layer through which light is transmitted to the eye; and when a colored solution is diluted with one that is colorless the shade lightens. But in neither case can it be taken for granted that the increase or reduction is strictly in proportion to the depth or dilution. The variation may be greater or less, according to the nature of the chromogen and solvent, nevertheless it is always safest to approximate, as nearly as may be, the standard to the sample both in shade and general composition, the former by tentative trials. The rule applies whether the liquids are viewed axially or transversely, in round tubes, flat cells, or glass wedges.

The depth of color of some organic bodies increases for a time after being brought into solution, and nearly all fade on long exposure to daylight. However, if the maximum color is reached within an hour and the fading does not begin to be apparent for a day or more, a comparison is not interfered with.

It should be observed that both standard and sample are in clear solution and at a uniform moderate temperature; that the glass of the comparison tubes is clear and colorless, and their internal diameter the same; and that the source of light is directly in line with the eye and tubes, and no side-lights interefere. The background to the tubes should be white paper or unglazed porcelain since a polished surface may reflect images.

Before making a final comparison it is well to rest the eyes for a short time on a screen of the color complementary to that of the tubes.

11. Impurities in reagents. No chemical can be purchased absolutely pure, nor is this necessary as a rule, for a distinction is to be made between such impurities as are objectionable for a particular analysis and others that cannot affect its accuracy. Thus, in the analysis of pyrite, even a considerable amount of sulfuric acid in the aqua regia used for solution will have no effect on the determination of the iron; while for the estimation of the sulfur, of course the acid and every other reagent should be free from this element. So it is well before commencing an analysis to consider what impurities may be in the reagents without detriment and what must be absent, and test for the latter.

The proportion of an interfering impurity in a reagent is best found by a blank or parallel determination. Another plan is to make two determinations on the sample to be analyzed, in one case taking double the weight of the other, but with equal quantities of the reagent in both. The difference between the results, calculated in percentages, is that due to the impurities in the reagent and can be used as a factor for the correction of future analyses made under like conditions.

The use of a volatile solvent that has been recovered from an organic analysis by distillation is often open to criticism since it may retain other volatile bodies difficult to remove by the ordinary process of purification, and that may interfere in future analyses.

As to the quality of the chemicals to be used in analysis it may be affirmed that the purest are ultimately the cheapest. The impurities in a crude chemical are apt to be of the most varied nature, and there is always an uncertainty as to whether some unsuspected one may not tend to vitiate or at least disturb the normal conduct of a determination.

12. Calculation. The most recent official tables of atomic weights are doubtless nearest correct and should be employed exclusively. The table is revised annually and is usually published in two divisions; in one the basis is hydrogen as unity, oxygen being 15.976, and in the other the basis is oxygen at 16, hydrogen becoming 1.008. Since one is the counterpart of the other there will be no difference whatever in results calculated entirely by either table, or at most an inconsiderable variation from the rounding off of the values of the different elements at the first or second decimal place.

It may seem superfluous to recommend that every computation should be verified by a repetition, yet it is surprising how frequently a simple arithmetical problem is missolved. One should early acquire the habit of corroborating every observation — twice noting the label of a reagent bottle or the reading of a burette or the rider-scale; reckoning a weight from the gaps in the weight-box, then from the weights on the pan; in short, checking up his work wherever possible.

A common oversight is that of not taking into account all the atoms when dividing a molecule; thus, a molecule of ferric oxide (Fe_2O_3, mol. wt. 112) contains *two* atoms of iron or $\frac{112}{160}$ of its weight. After writing out an equation one should check off the right-hand side against the left, to make sure that every atom appears in both.

Of a mixture that is mainly organic, certain inorganic constituents may be soluble in water and therefore be included in both the aqueous extract and the ash. With such material the residue from the watery extract should be calcined and the residue deducted from the weight of the ash of the material itself.

Of all the foregoing, the only errors that cannot be avoided in obvious ways, at least to a great extent, are the solubility of precipitates and their alteration on heating, for which the method should have made provision, and the solubility of glass and porcelain in the analytical solutions, which should not greatly influence the results provided the vessels are of a resisting quality.

The student will be fortunate if he progresses far without encountering difficulties and anomalies quite enough to tax his patience. Through neglect of a seemingly unimportant detail, a simple operation, ordinarily successful,

may display a perverse inclination to go wrong; in spite of attempts at rectification the trouble persists or increases until he may be tempted to affirm that the laws of chemistry, commonly believed immutable, have been temporarily reversed expressly for his personal annoyance. Yet if the study is begun with the more simple analyses where the conditions admit of considerable modification without impairing their efficiency and the manipulations are such that no great expertness is demanded, he will soon acquire such a familiarity with the details of working as to foresee at what points and under what circumstances errors are liable to occur, and so forewarned, forearmed; or when an unexpected difficulty presents itself, to know and apply the proper means to overcome it. Given a well-tried method, a fair acquaintance with the principles of analysis, and reasonable dexterity in manipulation, a result that is erroneous or doubtful should be an exception.

PART 2.

EXERCISES.

REAGENTS.

The reagents employed in the following analyses are now manufactured by several European and American firms, of quite sufficient purity for analytical work; yet it is never the part of prudence to omit their examination, for in the chemical market the designation "C.P." is so elastic as to cover every grade from the crude to the most refined. When it is difficult to purchase a chemical of the proper quality, the student will find it instructive to prepare a quantity synthetically or purify the commercial article.

Most of the salts described below are to be dissolved in distilled water and the solutions *diluted* to the strength specified. No strictly uniform system of moderate concentration can be adopted since the solubilities of the various reagents differ so greatly.* A decimal system is probably as convenient as any—one part of the reagent in ten parts of water, and where the solubility will not permit of this strength, in twenty, thirty, etc., parts water. Sparingly soluble reagents are conveniently made up as saturated solutions, a layer of the reagent covering the bottom of the bottle.

The solutions are preserved in chemical-glass (lead-free) bottles provided with glass stoppers and protected from dust and fumes by caps or inverted beakers. The labels are best molded or etched in the glass, though paper ones will answer if given a coat of white varnish or washed with a solution of paraffin in gasoline. The stoppers and bottles should be numbered conjointly to prevent interchange, as no two ground stoppers will accurately fit the neck of one bottle. Solutions of caustic potash or soda will firmly cement the stopper to the neck if the bottle is left unopened for some time; interposing a strip of thin platinum foil will prevent this, or a closely fitting glass cap may be substituted for the stopper.

Hydrofluoric acid and solutions of the caustic alkalies and their carbonates are best kept in bottles of platinum, silver or ceresin. Black glass protects silver solutions, etc., from decomposition by light; amber glass is less efficient. Reagents used in the solid form are kept in wide-mouth (salt-mouth) bottles and dispened with a horn spoon, while insoluble precipitants, such as certain metallic oxides and carbonates, are kept for use suspended in water.

Of solutions acting strongly on glass and those that decompose or ferment on standing it is better to dissolve about the required weight of the compound just before using. The concentration of a saturated aqueous solution of hydrogen sulfide is so small and it so early decomposes on keeping that it is usually better to transmit a current of the gas through the liquid to be precipitated than to depend on the hydrogen sulfide water.

In most cases the reagent alone is dissolved in water or other simple solvent, but a vehicle in the form of another chemical is sometimes incorporated in the solution for specific reasons. If the adjuvant is to take part in the reactions of the principal, the object of its introduction may be to assist in solution or precipitation; to change the composition of a precipitate to one more stable or of an aggregation easier to filter and wash; to cause or aid in the solution or precipitation of an associated body, or to prevent its solution or precipitation,

* Chem. News, 1890—1—245.

etc. If taking no direct part in the reactions, the purpose may be that of effecting the solution of the insoluble or sparingly soluble principal; to diminish the solubility of a precipitate or residue; to induce an alteration of the physical structure of a precipitate; to prevent decomposition, coagulation, putrefaction, or crystallization of the principal; or by its superior affinity for oxygen or carbon dioxide to preserve it from alteration through contact with the air, etc.

Many of the reagents in common use are extremely poisonous, not only when taken internally, but even on coming in contact with an abrasion of the skin or a mucous membrane, notably potassium cyanide, arsenic compounds, chloracetic and hydrofluoric acids. The vapors of hydrocyanic and hydrofluoric acids, arsine, the halogen, hydrogen sulfide, etc., undiluted by air are active poisons, and very deleterious to the respiratory organs even when considerably diluted. As many serious and not a few fatal accidents have come about through carelessness, the student is urged to be continually on his guard in this respect. And great care should be taken when using ether, gasoline, and such light volatile bodies, as their vapors are very diffusive and may catch fire at a considerable distance from the liquids.

To prepare a volume V of a solution whose specific gravity shall be d, by dilution of a volume X whose specific gravity is a, the specific gravity of water being b. The volume of the original solution is found from the equation $X = V\frac{d-b}{a-b}$, and the volume of water to be added to X is $V - X$.

Conversely, to dilute a certain volume V of a liquid of a specific gravity a to one of a lower gravity d, the equation reads $X = V\frac{a-b}{d-b}$; X being the volume of the diluted solution and $X - V$ the volume of water to be added.

If a grams of a solid is contained in b grams of a solution, and X is the weight of the solid in one Cc. of the solution, then $X = \frac{a}{b-a}$.*

Alcohol. C_2H_6O.

1. Absolute alcohol. Prepared by the fermentation of sugar; rectified, and freed from water by distillation from a highly hygroscopic solid. It is a colorless volatile liquid of agreeable odor, and mixes in all proportions with water and ether. When anhydrous it has a specific gravity of .794, solidifies at −130°, and boils at 78.4°.

2. Commercial. Sold as containing 95 per cent, but is often found to assay only 90 to 94 per cent, with 6 to 10 per cent of water, and traces of organic acids, aceton, fusel oil, aldehyd, etc.

3. Proof spirit. Has a gravity of .920 and contains 49.24 per cent by weight or 57.06 per cent by volume of alcohol.

The commercial 95 per cent article is sufficiently pure and strong for most analytical purposes; it should completely volatilize without an unpleasant odor, and dissolve pure caustic potash without acquiring at the time more than a light yellow color. Fusel oil is detected by the silver nitrate test.

Commercial alcohol invariably contains a little free acid, aceton, and aldehyd. No process is known by which the last two can be entirely removed; the process of Waller † giving a fair purification is as follows. Powdered potassium permanganate is slowly stirred in the alcohol until the color has become a deep purple; after standing until all the manganese has been deposited as hydrated peroxide, the alcohol is decanted and dis-

* Journ. Amer. Chem. Socy. 1897—587.

† Chem. News, 1890—1—53.

tilled, with the addition of a little calcium carbonate, from a flask with a fractionating column. The distillation should be slow and the first and last fractions rejected.

Alcohol strictly neutral in reaction is required for dissolving fatty acids to be titrated by a standard alkali. To commercial alcohol is added a few drops of phenol-phthalein or turmeric solution and dilute solution of caustic potash dropped in until the reaction has become distinctly alkaline, then more alcohol is dropped in until the red color has almost disappeared.

Ammonium chloride. NH_4Cl, 53.522.

(Sal-ammoniac.) White crystals, soluble in three parts of cold and 1.4 parts of boiling water. As purchased it generally contains some insoluble matters, though yielding a reasonably pure solution. Recrystallization is advisable when the salt is to be used for the determination of the alkalies in silicates; the filtered solution is evaporated up to the point of crystallization, and while cooling is constantly stirred that small crystals may form.

The salt should volatilize completely when heated on platinum foil, and be free from sulfate.

Ammonia. NH_3, 17.064.

A solution of gaseous ammonia in water, one volume of water at zero and 760 Mm. of mercury absorbing about 1100 volumes of the gas.

Ammonic hydrate, NH_4OH, 35.08. As purchased, the usual specific gravity is .9[illegible]0. The solution should be colorless, leave no residue on evaporation, and give no precipitate with nitric acid and silver nitrate (chlorine), barium chloride (sulfuric acid), or hydrogen sulfide (lead, etc.).

One gram of the solution of .900 at 15° Cent. contains .283 gram of NH_3, or .581 gram of NH_4OH; one Cc. contains .255 gram of NH_3, or .524 gram of NH_4OH, and neutralizes .545 gram of HCl, .942 gram of HNO_3, or .733 gram of H_2SO_4.

Used to neutralize free acids and to precipitate the hydroxides of weaker bases. Both the concentrated solution and the tenth dilution are needed.

Ammonium carbonate.

As found in the market it approaches the formula $3NH_3.2CO_2.H_2O$ or $N_3H_{11}C_2O_5$. It should volatilize completely when heated on platinum foil, and after dissolving in an excess of dilute hydrochloric acid give no turbidity with barium chloride.

Used for neutralization, and to precipitate the carbonates of calcium, barium, lead, etc. The solution is made up just before use by dissolving in water containing a little ammonia and filtering.

Ammonium oxalate. $(NH_4)_2C_2O_4.H_2O$, 142.116.

Colorless needles soluble in about 25 parts of cold water. Generally quite pure, but may contain a trace of lead or calcium; may be purified by recrystallization from hot water. Should leave no residue on ignition.

Solution, one part in 25 of water. Used to precipitate calcium, lead, and a few other metals, and as a standard reducing agent. One gram of calcium oxide is precipitated by 2.535 grams, and one gram of potassium permanganate is reduced by 2.2488 grams of the crystallized salt.

Barium chloride. $BaCl_2.2H_2O$, [illegible]4.332.

Colorless transparent crystals soluble in 2.4 parts of cold, and 1.3 parts of hot water. Prepared by dissolving barium carbonate in an insufficiency of hydrochloric acid for entire solution and crystallizing after filtration; or may be precipitated as a powder by adding alcohol or concentrated hydrochloric acid to the strong aqueous solution. Used almost exclusively for the determination of sulfuric acid. Solution, one part of the crystallized salt in ten parts of water. One gram of H_2SO_4 is precipitated by 2.491 grams of the crystallized salt; one gram of SO_3 by 3.052 grams; and one gram of sulfur (converted into sulfuric acid) by 7.619 grams.

Barium hydrate. $Ba(OH)_2.H_2O$, 315.544.

The crystals are soluble in about 20 parts of cold water. Used as an absorbent for carbon dioxide from a mixture of gases, as a precipitant for the weaker bases in separations, and to remove carbon dioxide from volumetric solutions of the caustic alkalies. One gram of sodium carbonate (Na_2CO_3) is rendered caustic by 2.974 grams of the crystals and one gram of K_2CO_3, by 2.283 grams.

Battery Fluid.

The liquid for exciting the battery described on page 249 is made by adding to 2000 Cc. of cold water, 400 Cc. of commercial oil of vitriol, and after cooling, dissolving 300 grams of commercial sodium chromate in the mixture.

Bromine. Br, 79.95.

A dark-red, corrosive, volatile liquid of specific gravity 2.99, solidifying at —25° Cent. Soluble in about 29 parts of cold water, and freely in alcohol, ether, and carbon disulfide. It is used as an oxidizing agent. A saturated solution is prepared by pouring some of the commercial article into a glass-stoppered bottle and washing with water once or twice; the bottle is then filled with water and after standing for a time, with occasional shaking up, is ready for use.

The bottle in which bromine is purchased should be opened with care in the open air. If the stopper cannot be removed, a cord may be tied round the neck, saturated with alcohol, and lighted; the heat will usually crack the neck so that the stopper can be broken out and the bromine poured into another bottle.

Calcium carbonate. $CaCO_3$.

Used in J. Lawrence Smith's method for alkalies in silicates. It must be free from potassium and sodium salts, frequent contaminations of the commercial product.

Prepared by dissolving calcite or chalk in dilute hydrochloric acid leaving a portion undissolved; then precipitating any magnesia or other base by milk of lime. The filtered liquid is heated nearly to boiling, precipitated by solution of *ammonium* carbonate, washed with hot water, and dried.

Chloroform. $CHCl_3$.

Trichlormethane. A colorless, volatile liquid, specific gravity 1.51 at 15°, boiling at 61°, and having a sweet taste and agreeable odor. It is soluble in about 200 parts of water, and mixes in all proportions with alcohol and ether. It should be neutral to litmus paper and leave no residue on evaporation. The commercial article (U. S. Pharmacopoeia 1900) is generally pure enough for most purposes; if not it is to be redistilled.

Chloroplatinic acid. $H_2PtCl_6.6H_2O$, 517.712.

A brown deliquescent solid very soluble in water and alcohol. If purchased it should be tested for sulfuric acid; also for sodium chloride by ignition and extraction of the residual platinum by dilute nitric acid, which after filtering should leave no residue on evaporation.

May be prepared as follows. Boil soft scrap platinum cut in very small pieces, in concentrated hydrochloric acid to clean them; weigh, and boil with aqua regia (three volumes of hydrochloric to one of nitric) until dissolved. Evaporate to dryness, dissolve in concentrated hydrochloric acid, and again evaporate. Dissolve the residue in water, ten cubic centimeters for each gram of platinum, and filter. The product is sufficiently pure for analytical purposes; it should be preserved in a glass-stoppered bottle away from dust and ammonia fumes.

Used as a precipitant for potassium and ammonia chlorides. Of a solution of the above strength, one gram of potassium chloride is precipitated by 13.1 Cc.; of potassium as chloride by 25 Cc.; of ammonium chloride by 18.2 Cc.; and of ammonia (NH_3) as chloride by 57.2 Cc. A large excess is always needed to lessen the solubility of the precipitates.

Ferrous sulfate, crystallized, $FeSO_4.7H_2O$, 278.182.

Transparent light-green crystals soluble in 1.64 parts of cold and .3 part of hot water, insoluble in alcohol.

The principal impurity of the commercial salt is ferric sulfate, removed by dissolving the crystals in water containing sulfurous acid and crystallizing, or by precipitating the concentrated aqueous solution by alcohol. Both the solution and the crystals are slowly perduced on exposure to the air.

Used as a reducing agent, and in volumetric analysis for standardizing permanganate solution. One gram of the crystallized salt contains .201365 gram of iron, and 8.7983 grams reduce one gram of potassium permanganate.

Hydrochloric acid. HCl, 36.458.

(Muriatic acid, chlorhydric acid, spirits of salt.) A colorless gas soluble in 1-500th of its weight or water at zero and 760 Mm. The specific gravity of the commercial acid is usually 1.200. It should be colorless, leave no residue on evaporation, and after concentration with the addition of a crystal of potassium nitrate, not be precipitated by a dilute solution of barium chloride. Free chlorine is shown by the blue color developed by dilute solution of potassium iodide and starch-paste, and arsenic by a brown color with stannous chloride and sulfuric acid.

It is of general use as a solvent for minerals, ores, oxides, etc Of the gravity of 1.200, one gram contains about .400 gram of HCl; one Cc. contains 480 gram. One Cc. neutralizes .739 gram of potassium hydrate; .527 gram of sodium hydrate; and .225 gram of ammonia (NH_3).

Hydrogen peroxide. H_2O_2, 34.016.

The commercial solution of the gas is usually stated to be of ten or twelve volume strength, meaning that one volume of the solution contains five or six volumes of the gas and evolves ten or twelve volumes of oxygen when decomposed by potassium permanganate. It slowly loses strength on keeping, less readily if the solution contains a small amount of an acid or a metallic salt.

Iron. Fe, 56.

The grade of iron wire known to the trade as "malleable wire" is made from the best quality of refined iron and may be considered, without sensible error, to contain 99.9 per cent of metallic iron and .1 per cent of slag, carbon, etc. Wire of this purity of a diameter of No. 21 American wire gauge, cut in six-inch lengths, is sold by dealers in chemicals. It should be cleaned before weighing by drawing between a fold of emery-paper.

When dissolved in hydrochloric or dilute sulfuric acid without access of air there is yielded a ferrous solution useful in standardizing volumetric solutions of an oxidizing nature. One gram of potassium permanganate is reduced by 1.7716 grams of metallic iron.

Lead carbonate. $PbCO_3$, 266.92.

A heavy white powder prepared by dissolving commercial lead acetate in water, adding a few drops of ammonia, and filtering. The filtrate is poured slowly and with constant stirring into a dilute solution of sodium carbonate, and the precipitate filtered, washed with hot water, and dried at 100°. This compound must not be confounded with painter's white lead which contains also the hydrate.

Nitric acid. HNO_3, 63.048.

Usual specific gravity 1.42. The colorless acid turns yellow on exposure to light, lower oxides of nitrogen being formed. It is a powerful oxidizer; used as a solvent for metals and to destroy organic matter. It boils at 121°.

Fixed bases are tested for by evaporation to dryness; chlorine by very dilute solution of silver nitrate; sulfuric acid by dilute solution of barium chloride, after concentration with a little potassium nitrate.

One gram of the acid of 1.42 contains about .700 gram of HNO_3.

One Cc. contains .994 gram of HNO_3, and neutralizes .888 gram of potassium hydrate; .631 gram of sodium hydrate; and .553 gram of ammonium hydrate.

Phenol-phthalein. $(C_6H_4OH)_2.C_6H_4CO:C:O$.

(Pron. fee″-nole-thal′-a-in, Stand. Dict., but variant.) Made by combining phthalic acid with phenol, removing a molecule of water by anhydrous phosphoric acid. Soluble in alcohol and ether, insoluble in dilute acids. Used as an indicator in alkalimetry, being colorless in acid and deep red in alkaline solutions. It is affected by carbonic acid, and unsuited for ammonia except with certain precautions.

Solution, one gram in 50 Cc. of alcohol; a drop or two suffices for a titration.

Potassium ferricyanide, $K_6Fe_2(CN)_2$.

Dark red crystals soluble in 2.5 parts of cold and 1.3 parts of hot water to an intense yellow solution. It is made by the oxidation of potassium ferrocyanide by chlorine.

Used as an indicator in volumetry, producing strongly colored precipitates with several metals. The solution should give no blue color with ferric compounds.

Solution for the spot indication of ferrous iron, about .050 gram in 50 cubic centimeters of water, to be freshly prepared before use. It is well to rinse the crystals with water before making up the solution in order to wash off the surface which may have become reduced to ferrocyanide by dust or fumes.

Potassium hydrate. KOH, 56.118.

A white deliquescent solid containing variable proportions of water up to 30 per cent or more. In the market are found three grades: "White" in sticks or granulated; "Purified by alcohol", and "Purified by baryta". The first contains considerable carbonic acid and sodium hydrate, with some silica, alumina, potassium sulfate, potassium chloride, etc., while the two latter are pure enough for ordinary use. The solution of one part of potassium hydrate in ten of water is to be preserved in ceresine or silver bottles. One gram of the anhydrous compound neutralizes .650 gram of hydrochloric acid; 1.124 gram of nitric acid; and .874 gram of sulfuric acid.

Potassium iodide. KI, 165.96.

Crystallizes in milk-white cubes soluble in .8 part of cold water and .5 part of hot water. Used in volumetric analysis to aid the solution of iodine in water, and as an inter-

mediate in the titration of free chlorine by thiosulfate. The pharmaceutical article is pure enough for most purposes.

Potassium permanganate. K_2MnO_4, 316.22.

Dark purple prisms with a bronze iridescence, soluble in 16 parts of cold and 3 parts of hot water. Purified by recrystallization from an aqueous solution, after filtration through asbestos or gun cotton. The aqueous solution slowly decomposes on standing; *e. g.*, a solution of four grams in a liter of water lost two per cent of its oxidizing power in 30 days.

Used in volumetric analysis, the decinormal solution containing 3.162 grams per liter. One gram contains .253 gram of oxygen in excess of that forming protoxides with the potassium and manganese. One gram of iron is converted from the ferrous to the ferric state by .56444 gram of permanganate; one gram of crystallized ferrous sulphate by .11365 gram; one gram of crystallized oxalic acid is decomposed by .5017 gram; one gram of crystallized ammonium oxalate by .44479 gram; and one gram of C_2O_4 by .7185 gram.

Potassium sulfocyanide. KCNS, 97.22.

(Potassium thiocyanate or rhodanate.) Transparent colorless crystals, very hygroscopic and soluble in water. The clear solution after acidification by nitric acid should not be troubled by silver nitrate, nor be colored red on acidification by pure hydrochloric acid (Fe_2Cl_6)*. Used as a precipitant for silver and copper, and as a volumetric solution for the determination of the former. Solution, one part in ten of water.

One gram precipitates .654 gram of copper (in presence of a reducing agent), and 1.109 grams of silver.

Pyrogallol. $C_6H_3(OH)_3$.

(Trioxybenzol, pyrogallic acid, pyrogallin, pyrrol.) The pharmaceutical product is usually pure enough for the purpose here desired—the absorption of oxygen from a mixture of gases. Five grams is dissolved in 15 Cc. of water and the solution mixed with 80 Cc. of water containing 80 grams of potassium hydrate. It should be made up just before using.

Ferrous potassium tartrate has been proposed as a substitute.

Silver nitrate. $AgNO_3$, 169.96.

Crystallizes in colorless anhydrous plates soluble in less than its own weight of water. The pharmaceutical salt is sufficiently pure. Used to precipitate the halogens, phosphoric and arsenic acids. Solution, one part in ten of water, to be kept in a dark place free from dust. One gram precipitates .208 gram of chlorine.

Sodium ammonium phosphate. $NaNH_4HPO_4.4H_2O$, 209.194.

Soluble in 6 parts of cold and one part of hot water; the usual impurities are a little calcium or magnesium phosphate; to eliminate these, the salt is dissolved in 20 parts of water containing a little ammonia, and filtered after standing for an hour or so. As the solution strongly attacks glass it should only be made up shortly before use.

The salt serves to introduce phosphoric acid and ammonia into a solution for the precipitation of magnesium, manganese, or zinc salts as their ammonium phosphates. One gram of the crystallized salt precipitates .193 gram of magnesia; .339 gram of manganese protoxide; and .339 gram of zinc oxide. With the two latter a large excess is needed to induce crystallization.

Sodium carbonate. $Na_2CO_3.10aq$, 286.26. Na_2CO_3, 106.10.

The anhydrous salt is most used in analysis and may be prepared quite pure by the process of Reinitzer.† He dissolves sodium bicarbonate in water at 80° to saturation and filters. On cooling to 10° to 15° the salt $Na_2CO_3 + NaHCO_3$ separates; this is washed by a little cold water by decantation, dried, and ignited gently in a platinum crucible.

As purchased, the so-called "dry sodium carbonate" is really of the grade known as "mono-hydrated", containing about 85 per cent of Na_2CO_3, and 15 per cent of carbon dioxide and water. The usual impurities are silica, alumina, chlorine and sodium sulfate, for which, in the determination of any of these compounds, the reagent must be tested and a correction made if found present in more than traces.

Used as a precipitant for many metals, for neutralizing free acids, and as a flux to decompose minerals insoluble in acids, notably the silicates. One gram of anhydrous sodium carbonate neutralizes .687 gram of hydrochloric acid, 1.188 of nitric acid, and .994 of sulfuric acid; and unites with .569 gram of silica.

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* Chem. News, 1891—1—150.

† Chem. News, 1895—1—31.

Sodium chloride. NaCl, 58.5.

Common salt crystallizes in cubes with recessed faces. It is soluble in 2.78 parts of water at 15°, and 2.53 parts at 100°, the increase in solubility with rise of temperature being less than in most other salts. It is insoluble in alcohol and strong acids.

Ordinary table salt is purified by dissolving to saturation in cold water with the addition of a few drops of sodium carbonate solution to precipitate the earthy salts, filtered, and the filtrate compounded with half its volume of strong hydrochloric acid. The liquid is decanted from the precipitated salt, which is drained and dried on the water bath. The mass is then powdered and heated to dull redness in a platinum dish.

The solution should give no turbidity with barium chloride or sodium carbonate, and not more than a faint red color with potassium sulfocyanide and hydrochloric acid. Its principal use is as a volumetric solution for the assay of silver compounds.

Sodium hydrate. NaOH, 40.053.

(Sodium hydroxide, caustic soda.) In most respects this compound is similar to potassium hydrate and a corresponding grade of one may usually be substituted for the other. A very pure article is for sale at a moderate price, made by oxidizing metallic sodium by water and evaporating the solution in a silver vessel. Wollney states that the usual impurities of the commercial article, sodium carbonate, nitrate and sulfate, are insoluble in a 50 per cent solution of the hydrate.

Sodium hydrate has about 1.4 times the neutralizing power of potassium hydrate toward a given acid. One gram of anhydrous sodium hydrate neutralizes .910 gram of hydrochloric acid, 1.573 gram of nitric acid (HNO_3), and 1.224 gram of sulfuric acid.

Sulfuric acid. H_2SO_4, 98.066.

(Oil of vitriol.) According to Pickering* the specific gravity of 100 per cent acid is 1.833937 at 17.9° Cent. An acid containing 10 per cent of H_2SO_4 has a gravity at 15.5° of about 1 07. The usual gravity of the acid as purchased is 1.84, a heavy oily liquid boiling at 338°, very corrosive, deliquescent, and evolving great heat on dilution with water. Should be colorless or only slightly brown. The diluted acid must give no color to potassium iodide and starch paste (HNO_2), and no precipitate with hydrogen sulfide (lead, etc.). Nitric acid is shown by a brown ring at the junction with a strong solution of ferrous sulfate; sulfurous acid by diluting and adding a drop of a dilute solution of potassium permanganate which should not be immediately decolorized; iron, by testing with dilute solutions of potassium sulfocyanide and ferricyanide; and arsenic, by the brown coloration of the diluted acid when treated with stannous chloride and tin.

Used as a solvent for some metals and their oxides, indigo, cellulose, casein, etc., and to precipitate lead and the earths.

Of the specific gravity of 1.84 it contains about 95 per cent of H_2SO_4 (an acid of 99.6 per cent has the same gravity); one gram contains about .950 gram of H_2SO_4, and one Cc. 1.748 grams. One Cc. neutralizes 2.000 grams of potassium hydrate; 1.428 grams of sodium hydrate, .608 gram of ammonia (NH_3); and precipitates 2.735 grams of baryta; 1.000 gram of lime; and 3.687 grams of lead.

By adding 58 cc. of the acid of 1.84 gravity to one liter of cold water is furnished a solution containing about ten per cent of H_2SO_4.

Sulfurous acid. H_2SO_3, 82.092.

Sulfurous anhydride (SO_2) is a colorless gas, specific gravity 2.23. One volume of water at zero dissolves 79.8 volumes, and at 20° 39.4 volumes. The solution loses strength and oxidizes on standing.

The solution is prepared by leading into cold water the gas generated from sodium bisulfite and dilute sulfuric acid, or copper turnings heated with concentrated sulfuric acid. The solution should smell strongly of the gas and leave no residue on evaporation. Used as a reducing agent.

Water. H_2O, 18.016.

Few natural waters are so free from suspended or dissolved matters as to be fit for quantitative analysis, so recourse is had to the simple mode of purification known as distillation. The still for boiling the water and the condenser for liquefying the steam as shown in Fig. 136 are too well known to need an extended description.

The body of the still is a copper tank surmounted by a beak or capital which is fitted to the neck of the still by friction, or the two are provided with flanges and may be

* Chem. News, 1892—1—14.

bolted together, interposing a rubber gasket. The water in the still is boiled by a gas burner or other source of heat, or by a coil of steam pipe in the interior. From the beak the steam enters a coil of block-tin pipe wherein it is condensed, the water flowing out from the lower end of the coil projecting from the tank Surrounding the coil is a metal tank containing cold water, which is continuously renewed as it absorbs the heat of the steam, entering through a pipe at the bottom and leaving near the top.

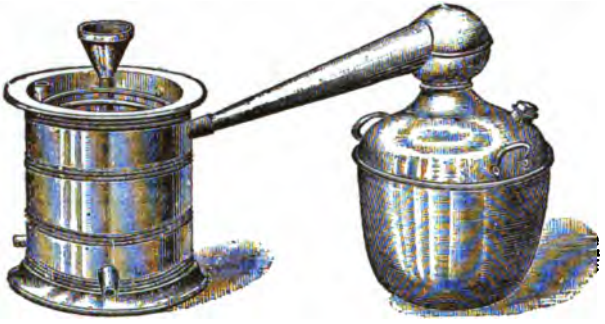

Fig. 136.

The still and head are coated interiorly with tin, and a tin pipe forms the worm since this metal is practically unaffected by water, which is not the case with other common metals and glass.

It will be seen that this apparatus, economically considered, is very imperfect, and several improved apparatus are now on the market, so modified as to operate automatically and produce a greater yield of distillate in proportion to the volume of gas burned. Usually the still is broader and shallower and the coiled-pipe worm is replaced by a thin wide tube incased in a box of the same shape. The cooling water circulates between the tube and box entering at the bottom, its temperature increasing as it rises, until at the top it is almost at the boiling point. From thence a part flows into the still through a constant level (page 27), saving the time and fuel needed to heat cold feed-water to the boiling point as in the ordinary form of still.

If the top be closed and the hot water near the surface be raised quite to the boiling point the condenser itself may be utilized as an auxiliary still by directing the steam generated into its worm. This is accomplished in the "Domestic Still". The steam as it leaves the still passes to the worm through an aspirator (on the principle of the vacuum pump, page 93), drawing in with it steam from the condenser; this is generated, not by raising the water to full 100°, but through the lowering of its boiling point by the creation of a partial vacuum in the condenser by virtue of the aspirator.

The first portion of the distillate is rejected as containing the gases always present in natural water, etc., and the distillation is stopped before all the water has evaporated.

Distilled water should be neutral, tasteless, colorless, and odorless; leave no residue or only a trace on evaporation; and not be clouded by solutions of barium chloride, silver nitrate, or hydrogen sulfide. Minute traces of organic matter, carbon dioxide, nitric acid, etc., are of no consequence in general analysis; for the few special determinations where no organic matter whatever may be present, the ordinary distilled water is rectified over potassium permanganate or chromic acid and sulfuric acid. Ammonia-free water is easiest obtained by boiling ordinary distilled water in an open wide-mouth flask until a test shows that all free ammonia has passed off.

Distilled water is always to be preserved in chemical-glass bottles, never in stoneware jugs.

Whenever water is mentioned in the following exercises, distilled water is to be understood.

Zinc. Zn. 65.40.

The bluish-white metal is soluble in most acids, giving hydrogen-gas with hydrochloric and dilute sulfuric acids. Some commercial varieties are remarkably pure. For analytical use it should contain very little carbon, iron, lead, or arsenic. The first two are tested for by dissolving the zinc in dilute sulfuric acid and titrating by a weak solution of potassium permanganate; lead remains undissolved, and arsenic is volatilized as arsine, shown by Marsh's or other test.

A convenient foliated form is left when the zinc is melted in a clay (not graphite) crucible and poured into water. The metal in stick, granulated, and powdered form is now on the market.

Used to reduce per- to proto-salts in acid solution, and to decompose some metallic compounds with separation of their bases in the metallic form, as those of lead, silver or copper. It is also of general use as a reducing agent.

EXERCISES FOR PRACTICE.

The following exercises illustrate many of the principles and expedients employed by the analyst and have been chosen from the simpler problems he is called on to solve. The methods have been selected primarily with reference to their requirement of but little skill and experience on the part of the operator and of few special or complicated forms of apparatus; for this reason, there may be found in the standard works other methods that are superior in some respects to those here given, and it will be well for the student, after acquiring some familiarity with the physical and chemical properties of the substance treated, to essay one or more of them as circumstances permit.

Directions have been given in detail, though it is not to be inferred that any deviation therefrom is unallowable — on the contrary, they are intended as a guide rather than a rule, except where it is obvious that they must be strictly adhered to.

The student is advised to make every analysis in triplicate as the time consumed does not greatly exceed that for a less number, and confidence in his work is engendered by a close agreement of three results; moreover, should an accident happen one, the other two may be carried forward without the delay incident to starting the analysis afresh.

A knowledge of the capabilities of the balance used and the limits of its sensibility under different loads, the closeness of the agreement of the weights one with another, and a verification of the graduation of the volumetric vessels, must be secured before any analytical work is undertaken; as otherwise there is always a feeling of uncertainty and a temptation to charge unsatisfactory results to their inaccuracies. The student should personally acquire this information, as at the same time he becomes familiar with the manipulation of the various instruments.

Wherever two exercises are included under one number, the principles of the two are similar and the one most convenient may be chosen for analysis.

EXERCISE 1 — ALCOHOL.

Determination by Specific Gravity.

The density of absolute alcohol at 15.5° is .7946, rising as it is diluted with water. As a contraction in volume takes place when the two liquids are mixed, the published tables of the percentages of alcohol corresponding to different specific gravities have been compiled from direct experiments on mixtures of known volumes.

The commercial grade of alcohol sold as '95 per cent' contains from 90 to 95 per cent by weight. Its specific gravity is found from the weight of a convenient volume as compared with that of an equal volume of water, at a standard temperature, usually 15.5° Cent.* As the temperature of the laboratory is usually not less than 20°, dew is condensed on a vessel holding a liquid at a lower temperature and prevents an exact weight being taken; so instead of the pyknometer or specific gravity flask it will be found more convenient to note the loss in weight suffered by an immersed solid as compared with its weight in air, this being the weight of an equal volume of the surrounding liquid.

* Allen, Coml. Org. Anal. 1—92.

Over the left-hand pan of the balance is placed the wooden bridge, Fig. 137, supporting as wide a beaker as will easily pass between the wires without touching either. In the beaker, about half way down, there is hung by a silk thread or a fine wire a clean and smooth piece of metal weighing from 50 to 100 grams. The weight is accurately observed, taking care that the metal does not touch the beaker, nor the pan wires the beaker or bridge.

Two flasks of about the same capacity as the beaker are filled, one with the alcohol to be tested, the other with distilled water; they are immersed in ice-water until the temperature of the liquids has fallen below 15°. The flask containing the alcohol is removed from the bath, and when the temperature of the alcohol has risen to about 14°, the beaker is filled, and the plummet weighed, to within a milligram only, since the vibrations of the beam are impeded by the density of the liquid.

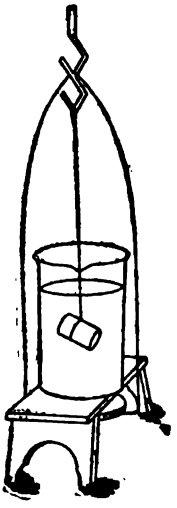

Fig. 137.

The beaker is emptied, the plummet dried, and its weight in the water found under the same conditions that obtained with the alcohol, but care must be taken that any air-bubbles are removed (by a camels-hair pencil when in the water) that may adhere.

Calculation. Let the weight of the plummet in air be A; in alcohol, B; and in water, C. Then $A-B$ is the weight of a volume of alcohol, and $A-C$, that of a volume of water equal to the volume of the plummet; therefore $A-C : A-B :: 1 : x$, the specific gravity of the alcohol. In the table below, x will probably be found to lie between two of the gravities there given. The one next lower is subtracted from it and the difference divided by the corresponding number in the column headed 'Decrease in specific gravity.' The quotient is subtracted from the percentage given in the second column, the result being the percentage of alcohol by volume. The percentage by weight may be obtained by multiplying the percentage by volume by .7946 and dividing the product by the observed specific gravity.

Example. A brass cylinder weighed in air 99.840 grams; in alcohol at 15.5°, 90.091; and in water at 15.5°, 87 941 grams.

$99.840 - 97.941 : 99.840 - 90.091 :: 1.0000 : x$. $x = .8193$. From the table, $.8193 - .8164 = .0029$; and $.0029 \div .0035 = .83$ Hence $95.00 - .83 = 94.17$ per cent by volume, or 91.33 per cent by weight.

Table of the percentage of absolute alcohol in commercial alcohol by volume corresponding to specific gravities at 15.5° Cent. against water at 15.5° (Squibb).

Specific Gravity.	Per Cent of Alcohol.	Decrease in Sp. Gr.	Specific Gravity.	Per Cent of Alcohol.	Decrease in Sp. Gr.
.8496	85	....	.8237	93	.0035
.8466	86	.0030	.8199	94	.0038
.8434	87	.0032	.8164	95	.0035
.8408	88	.0026	.8125	96	.0039
.8373	89	.0035	.8084	97	.0041
.8340	90	.0033	.8041	98	.0043
.8305	91	.0035	.7995	99	.0046
.8272	92	.0033	.7946	100	.0049

EXERCISE 2—A. LEAD CARBONATE.

Determination of Carbon Dioxide.

Pure lead carbonate (page 209) is a white powder, unaltered at 100°, but converted into the protoxide at a temperature approaching redness, carbon dioxide escaping — $PbCO_3 = PbO + CO_2$.

Lead protoxide is a white powder, yellow while hot. It melts at a bright red heat, at which temperature it is reduced to metallic lead by carbon, carbon monoxide, or gaseous hydrocarbons.

The determination of carbon dioxide is made by igniting the carbonate, the loss in weight being that of the carbon dioxide escaping.

Clean a small porcelain crucible and cover, and heat gently over a Bunsen burner. Transfer to a desiccator, and when cold weigh to within one milligram.

Remove the cover and place it on the scale-pan beside the crucible. Add a two-gram weight to those in the pan, and with a spatula or horn spoon drop into the crucible a little more of the powder than will restore equilibrium; cover the crucible and dry in the water oven or air-bath at 100° for half an hour. Cool in the desiccator and weigh accurately.

Heat the covered crucible over a small flame gradually increased, until the bottom of the crucible appears slightly red, and the powder turns brown, then yellow or nearly so. Slowly diminish the heat, cool in the desiccator and weigh. Repeat the ignition and weighing until two consecutive weights do not differ by more than one milligram.

The heat applied must not be so great as to fuse the lead oxide, and the crucible must be heated and cooled slowly to prevent fracture. The point of the blue flame should never reach the bottom of the crucible.

Calculation. The weight of the lead carbonate less the weight of the lead oxide is the weight of the carbon dioxide expelled. Also — Weight of the lead carbonate : weight of carbon dioxide : : 100 : percentage of carbon dioxide.

Example.

Weight of	Grams.
Crucible and lead carbonate	25.574
Crucible alone	23.038
Lead carbonate	2.536
Crucible and lead oxide	25.154
Crucible alone	23 038
Lead oxide	2.116
Carbon dioxide	.420
Percentage of carbon dioxide	16.56
Theoretical percentage	16.49

B. FERROUS SULFATE.

Determination of Iron.

On heating crystallized ferrous sulfate ($FeSO_4 7H_2O$), it loses first its water of crystallization, then sulfurous and sulfuric anhydrides, and ferric oxide remains —

$$2FeSO_4\ 7H_2O + \text{heat} = 14H_2O + SO_2 + SO_3 + Fe_2O_3.$$

From the weight of the residual ferric oxide is calculated that of the iron it contains and the percentage of iron in the crystallized salt.

Select small dry unoxidized crystals prepared according to the directions on page 208. Heat a covered platinum crucible to redness, cool in a desiccator and weigh. Introduce about two grams of the crystals and weigh accurately. Heat the covered crucible over a very low flame until the water is expelled, then support the crucible as shown in Fig. 94 and gradually increase the heat to dull redness. The expulsion of the sulfur oxides is known to be complete when the color has changed to a uniform dark red. It is well to stir the powder occasionally with a thin platinum wire. Cool the crucible in the desiccator and weigh. Again ignite the uncovered crucible, cool and weigh as before, repeating if the two weights do not agree.

Calculation. One molecule of ferric oxide (160) contains two atoms of iron (112); hence 160 : 112 : : weight of ferric oxide: weight of iron it contains.

Also, Weight of crystallized salt : weight of iron contained : : 100 : Y, the percentage of iron contained.

Example:

	Grams.		Grams.
Crucible and salt	18.775	Crucible and ferric oxide	17.347
Crucible empty	16.774	Crucible empty	16.774
Ferrous sulfate	2.001	Ferric oxide	.573

160 : .112 : : 573 : X. $X = .4011$ gram iron.

2.001 : .4011 : : 100 per cent : Y. $Y = 20.04$, the percentage of iron in the crystallized ferrous sulfate.

Theoretically, 278.182 (ferrous sulfate) : 56 (iron) : : 100 : Z. $Z = 20.13$ per cent.

EXERCISE 8 — SODIUM CHLORIDE.

Determination of the Atomic Weight of Chlorine.

On evaporation of a solution of sodium chloride with an excess of nitric acid it is converted into sodium nitrate —

$$3NaCl + 4HNO_3 = 3NaNO_3 + NOCl + Cl_2 + 2H_2O.$$

Sodium nitrate is a crystalline transparent salt, easily soluble in water, slightly hygroscopic, and melting at 330°. It decomposes at a dull red heat evolving oxygen.

Clean and dry a crystallizing dish about three inches in diameter, cover with a watch-glass, and weigh. Introduce about four grams of pure sodium chloride (page 211), heat in the air bath to 110° for a half hour, cool in the desiccator, and weigh exactly.

Place the dish on the water bath, remove the watch-glass, and add 25 Cc. of water and 10 Cc. of concentrated nitric acid. When the solution has evaporated to a small volume add 10 Cc. of water and evaporate to complete dryness.

Wipe the exterior of the dish, heat in the air bath to about 120° for an hour, cover with the watch-glass, cool in the desiccator and weigh. Dissolve the residue in water and be assured that the conversion is complete by testing for chlorine by silver nitrate.

Calculation. Taking the atomic weights of oxygen as 16, sodium as 23.05, nitrogen as 14.04, and chlorine as X, since one molecule of sodium chloride is transformed to one molecule of sodium nitrate we have the proportion,

Weight of sodium nitrate found : weight of sodium chloride : : 85.09 (mol. wt. of $NaNO_3$) : $X + 23.05$ (mol. wt. of NaCl).

Example.	A.	B.	C.
Weight of dish and NaCl	45.7579	34.4927	47.0140
Weight of dish	41.7531	30.4227	43.0206
Weight of NaCl	4.0048	4.0700	3.9934
Weight of dish and $NaNO_3$	47.5819	36.3398	48.8283
Weight of dish	41.7531	30.4227	43.0206
Weight of $NaNO_3$	5.8288	5.9171	5.8077
Atomic weight of chlorine	35.41	35.48	35.46

EXERCISE 4—A. COFFEE.

Determination of the Extractive Matter.

Coffee is the seeds of any species of the genus *Coffea*, especially the *Coffea Arabica* Nat. Ord. *Cinchonaceae*. The seeds have the form of plano-convex pyrenes, and before exportation are decorticated and dried. The imports into the United States come chiefly from Brazil and Sumatra, of the Rio and Pedang varieties and a small proportion of genuine Java.

The berry is made up of a cellular structure of cellulose inclosing a complex mixture of an oil or fat, the alkaloid caffeine, tannic and caffeo-tannic acids, gum, and smaller amounts of sugar, inorganic salts, etc. The proportions vary considerably as shown in the following analyses made on dried material.

	Maximum.	Minimum.
Gummy matter and sugar	27.40	20.60
Caffeine	1.53	.64
Fat	21.79	14.76
Tannic and caffeo-tannic acids	23.10	19.50
Ash	4.90	3.80
Cellulose	36.40	29.90

By roasting, the water contained is reduced from about 11 to 3 per cent, part of the caffeine is driven off, and a part of the sugar changed to caramel, while a fragrant aromatic body is developed.

When the powder of roasted and ground coffee is exhausted by boiling water there are dissolved caramel, caffeic acid, caffeine, legumine, a volatile oil (caffeone), a little fatty matter, and some inorganic bodies mainly potassium phosphate. On evaporation the filtered decoction leaves a residue of about 22 to 28 per cent of the coffee, the average being about 24 per cent.*

The lower grades of coffee are sometimes adulterated with the dried and powdered root of the chicory (*Cichorium Intybus*), and wholly factitious beans have been manufactured on a large scale. On extraction as above, however, chicory leaves a much higher percentage of residue, approximating 70 per cent, so that any percentage greater than about 24 in a sample of ground coffee would indicate an admixture of chicory or other foreign matter. Assuming chicory to be the only adulterant, its proportion could be roughly calculated from the formula $X = 100\frac{d-b}{a-b}$, where X is the percentage of chicory in the

* Analyst, 1898—226.

mixture; *a*, the percentage of residue from chicory (70); *b*, the average percentage of residue from coffee (24); and *d*, the percentage of residue found in a mixture.

About an ounce of the roasted berries is ground to pass through a 20-mesh seive; five grams is quickly weighed and brushed into a large porcelain dish containing 200 Cc. of boiling water. The mixture is boiled for 15 minutes, allowed to settle, and the turbid liquid decanted from the coarse fragments into a 250 Cc. measuring flask. The residue is again boiled for five minutes with 50 Cc. of water and decanted into the flask.

The decoction is cooled to the temperature of the room in a stream of water, made up to the mark with cold water and mixed well. It is then filtered through a dry triple filter into a dry beaker, returning the filtrate until it passes clear or nearly so.

Three crystallizing dishes of about three inches diameter are weighed and 50 Cc. of the extract transferred to each by a pipette. After evaporation to dryness on the water bath, they are heated for 30 minutes in the water oven, cooled in the desiccator and weighed.

Calculation. The increase in weight of each dish corresponds to the soluble matter in $\frac{50}{250}$ of 5 grams of coffee (=1 gram), hence the increase multiplied by 100 is the percentage of soluble matter.

Example.

	A.	B.	C.
Weight of dish and residue	28 0750	22 4945	26.0965
Weight of dish	27.8360	22.2580	25.8575
Weight of residue	.2390	.2365	.2390
Percentage of soluble matter	23.90	23.65	23.90

B. GINGER.

The rhizome of the *Zingiber officianalis* nat. ord. *Zingiberaceae*. The plant is a native of tropical countries and several varieties are found in commerce—the Jamaica, African, East Indian, Cochin, etc. The rhizome is composed principally of starch, woody fiber, resin, volatile and fixed oils, and mineral matter with ten to fifteen per cent of moisture. The powder is sometimes adulterated with rice-starch, chalk, etc., but more frequently is fraudulently deprived of a portion of its essential oil by steeping in water, the residue being dried and sold for the unsophisticated article. A positive statement that a sample of ginger has undergone this degradation is admissible only when indicated by several different tests. One of these is the extraction of the powdered ginger by alcohol, evaporating and weighing the residue which should not fall below 4.8 per cent of the undried ginger.

The alcoholic extract contains the pungent or active principle *gingerol*, a viscid, odorless liquid of the consistency of treacle; extractive matter soluble in water; neutral and acid resins; small quantities of a red fat; wax; etc. Since a large part of the extractive is volatile even at ordinary temperatures, the evaporation should be conducted at as low a heat as possible and the residue weighed without delay. For this reason also, the results of the determinations may differ to a considerable extent.

The closed end of a test-tube three-fourths of an inch in diameter is softened in the flame of a Bunsen burner and drawn out to a small orifice. Absorbent cotton is tightly packed in to the height of about an inch, and a little alcohol run through to clear it of any soluble matter. A glass crystallizing dish or bottom of a beaker is dried and weighed. The tube is clamped to a retort stand as in figure 45, the dish beneath it.

Powdered ginger is put into a wide-mouth bottle until half full, and the bottle corked and shaken until all lumps are broken up and the powder thoroughly mixed. Five grams is weighed to within a milligram, and transferred to the tube by a square of glazed paper and a camels-hair pencil.

A narrow-necked flask holding 50 Cc. is filled to the brim with 95 per cent alcohol, then stopped with the finger and inverted over the tube, and the neck quickly lowered into it. The level of the alcohol in the tube slowly falls to the mouth of the flask and remains there until the flask is empty — this should take several hours, and it is best to nearly cover the dish with a watch-glass and allow the percolation to proceed over night.

The tincture is then evaporated to dryness on the water bath, taking care that the alcohol does not boil. The dish is wiped dry, allowed to stand in the desiccator until cool, and weighed.

Calculation. The weight of the residue times $\frac{100}{5}$ gives the percentage of the alcoholic extract.

Example. Five grams of Jamaica ginger treated as above —

Weight of dish and residue	30.764	23.986	26 796
Weight of dish	30.502	23.722	26.544
Weight of residue	.262	.264	.252
Percentage of extract	5.24	5.28	5.04

References. United States and American Dispensatories; Amer. Journ. of Pharm. 1879–519. Bulletin No. 13, U. S. Dept. of Agriculture, 1887.

EXERCISE 5 — UNREFINED IRON.

Determination of Silicon.

Pig- or cast-iron contains from 3.5 to 4.5 per cent of carbon, partly dissolved in the iron or combined with it, and partly free in the form of graphitic plates; small and variable proportions of sulfur, phosphorus, and manganese; and silicon up to 3 per cent or more, usually less in "white iron" than "gray iron".

When the metal is dissolved in dilute sulfuric acid most of the combined carbon, sulfur and phosphorus unite with nascent hydrogen and pass off as odorous gases; the iron and manganese with the remainder of the phosphorus dissolve; the graphite is unaffected; while the silicon is hydrated, the major portion dissolving. If this solution be treated with nitric acid, the ferrous is changed to ferric sulfate, and the remainder of the combined carbon and sulfur dissolve. On evaporation, nitric acid and water are expelled; the excess of the sulfuric acid becomes concentrated and abstracts the water from the hydrated silica (leucocone); and on treating the residue with dilute hydrochloric acid the ferric and manganous sulfates are dissolved leaving anhydrous silica mixed with graphite. After filtering, the graphite is burned away, leaving the silica ready to be weighed. From its weight, the percentage of silicon is calculated.*

* Drown, Trans. Amer. Inst. Mining Engineers, 7—346; Journ. Amer. Chem. Socy. 1886—547.

The iron should be in the form of drillings or turnings, well mixed and free from oil, rust and dirt. Weigh one gram on a small watch-glass and brush it into a small beaker. Dissolve in 25 Cc. of dilute sulfuric acid (1 to 10), and when effervescence ceases, oxidize with 5 Cc. of concentrated nitric acid. Remove the watch-glass covering the beaker and evaporate on the hot-plate until white fumes of sulfuric acid arise. Cool, add 10 Cc. of concentrated hydrochloric acid and 50 Cc. of hot water and boil until all the white ferric sulfate is taken up. Filter through a 9 Cm. paper and wash alternately with water and hot dilute hydrochloric acid until the washings show no red color with potassium sulfocyanide.

Heat a covered platinum crucible to redness, cool and weigh. Partially dry the filter on a tile or blotting paper, and place it in the crucible. Heat gently until the paper is charred, then burn it and the graphite as directed on page 103. The graphite requires upward of a half hour for its combustion at a red heat, stirring occasionally with a platinum wire. The remaining silica should be pure white.

Calculation.

SiO_2 (60.40) : Si (28.40) : : weight of SiO_2 : weight of Si. Weight of iron : weight of silicon : : 100 : per cent of silicon.

Example. Three portions of one gram each treated as above;

	A.	B.	C.
Weight of crucible and silica	12.1365	12.9985	15.4811
Weight of crucible	12.1005	12.9622	15.4453
Weight of silica	.0360	.0363	.0358
Percentage of silicon	1.69	1.71	1.68

EXERCISE 6—ETHER.

Determination of Alcohol.

Pure ethyl ether $C_2H_5.O.C_2H_5$ is a colorless, inflammable and very volatile liquid boiling at 34.6° and of a specific gravity at 15/15° of .719. It mixes in all proportions with alcohol, is soluble in about 12 parts of water, and dissolves about 1/35 its weight of water, more freely when containing alcohol.

The 'sulfuric ether' of commerce always contains a certain proportion of alcohol and water as impurities. There are three grades on the market; one prepared according to the U. S. Pharmacopoeia of 1880 and containing about 26 per cent of alcohol and varying amounts of water; another according to the U. S. P. of 1890 containing about four per cent of alcohol and one or two of water; and 'ether for anaesthesia,' as pure or purer than the latter.

1. Commercial ether parts with its alcohol when shaken with a sufficient proportion of water; the water also dissolves a portion of the ether, but none, of course, if previously saturated with ether.

2. If a measured volume of commercial ether be agitated with sufficient ether-saturated water, the diminution in volume of the former corresponds to the volume of alcohol extracted. The increase in volume of the water is not equal to the volume of alcohol entering it, on account of the contraction of the mixture.

Cold distilled water is tinted to a light violet by a weak solution of Hoffmann's violet in water, and about 30 Cc. is poured into a burette containing about 5 Cc. of ether. The burette is closed by the thumb and briskly shaken

for a few minutes. On standing for a short time the excess of ether will float on the surface of the saturated colored water.

Into a clean graduated measuring-tube or burette is tapped about 20 Cc. of the colored water and measured after standing for a short time. Then 20 to 25 Cc. of the sample of ether to be examined is run in from a pipette, holding the orifice against the side of the tube to prevent the liquids mixing to any extent. The tube or burette is closed by a smooth soft cork, and the dividing line and the surface of the ether are read. The dividing line is more easily discernible by the contrast in color.

The ether is emulsified by vigorous shaking, and the tube or burette stood upright for 15 minutes, and the volume of ether again read. The ether should be colorless — if tinted there is too great a proportion of alcohol to water, and another experiment should be made, previously diluting the sample with an equal volume of alcohol-free ether.

It is important, of course, that the temperatures of the liquid at the times of reading are practically the same, and in a room subject to draughts it is well to immerse the tube in a jar of water for a few minutes previous to each observation. Results are usually fairly accurate, the error minus and not exceeding one per cent.*

Calculation. The diminution in volume of the ether divided by the volume of the sample, and the quotient multiplied by 100 is the volume-percentage of alcohol contained. The product is to be doubled in cases where the original sample was diluted with an equal volume of pure ether.

Examples.

	No. 1.	No. 2.
Volume of water	19.8 Cc.	20.9 Cc.
Volume of ether	25.0 Cc.	25.0 Cc.
After extraction, volume of ether	24 2 Cc.	22.8 Cc.
Diminution in volume of the ether	.8 Cc.	2.2 Cc.
Percentage V/V of alcohol contained	3.2	8.8

EXERCISE 7 — ACIDIMETRY.

Preparation of Standard Acid and Alkali.

Standard Acid. An approximately normal solution of sulfuric acid is made by diluting the concentrated pure acid of commerce. Into a one-liter measuring flask about three-quarters filled with cold water is poured 29 Cc. of the acid of 1.84 specific gravity. When the mixture has cooled to the temperature of the room it is made up to the mark with water and well mixed. The solution will be slightly stronger than the normal (49.043 grams of H_2SO_4 per liter).

Standardizing. The exact strength or titre of the acid may be found in several ways of which one is here given.

A measured volume of the acid is neutralized by ammonia and evaporated to dryness. From the weight of the residual ammonium sulfate is calculated that of the sulfuric acid. Of course any non-volatile impurities in the acid or ammonia will vitiate the result.

Select a glass crystallizing dish (or bottom of a beaker, page 60) about three inches in diameter and rub the upper edge slightly with vaseline; cover with a light watch-glass and weigh. Note the temperature of the acid, and pipette 25 Cc. into the dish. Slowly add dilute ammonia until a narrow strip of litmus paper just turns blue. Rinse the paper and evaporate to dryness on the water-bath.

* Analyst, 2—98.

As soon as a film of crystals forms on the surface there is danger of loss by spattering, and one must continually agitate the dish until the salt solidifies.

Now add a few drops of ammonia, evaporate to complete dryness, and heat in the air-bath to 105° for a half-hour. Cover with the watch-glass, cool in the desiccator and weigh. The increase is $(NH_4)_2SO_4$ from which the H_2SO_4 is calculated by the proportion

Weight of $(NH_4)_2SO_4$: weight of H_2SO_4 : : 132.214 : 98.086.

and the weight of H_2SO_4 divided by 25 gives the weight in one Cc.

Example. Twenty-five Cc. of acid, diluted as above, evaporated with ammonia;

	A.	B.	C.
Weight of ammonium sulfate and dish.....	31.145	33.863	31.146
Weight of dish.....	29.419	32.136	29.417
Weight of ammonium sulfate	1.726	1.727	1.729
One Cc. of the acid contains.....	.05122	.05125	.05131

The average of the three results is .05126. The neutralizing power of this acid for potassium and sodium hydrates is found by multiplying this number by $\frac{112.236}{98.086}$ and $\frac{80.116}{98.086}$ respectively. The acid is poured into a dry glass-stoppered bottle labeled about as follows: "Approximately normal sulfuric acid. At.....degrees Cent. one Cc. contains.....gram of H_2SO_4 and neutralizes.....gram of KOH, and.....gram of NaOH, with.....as indicator. Date of standardization....."

The neutralizing power of normal acid decreases with rise of temperature *; if 100 at 15°, it will be 99.92 at 17.5°; 99.85 at 20°; 99.77 at 22.5°; 99.69 at 25°; 99.61 at 27.5°; and 99.52 at 30°.

Standard Potassium Hydrate. A solution is made up from the grade of caustic known as 'purified by alcohol,' and standardized by titration against the standard acid. Since the commercial potash contains a considerable proportion of water (often 30 per cent), a solution stronger than normal is made and tested, then diluted to the proper strength. About 100 grams of potash is dissolved in cold water and diluted to one liter; 50 Cc. of this solution is transferred to a beaker, diluted with water, and a few drops of phenol-phthalein added. A burette is rinsed with the standard acid and filled to the zero mark. The acid is cautiously run into the red titrate until the color is just discharged; the volume of acid required is V cubic centimeters.

Since of strictly normal solutions equal volumes react, we will calculate to what extent the alkali solution must be diluted to make it approximately normal. From the proportion $50 : V : : x : 1000$, we find that x Cc. of the alkali would be neutralized by 1000 Cc. of the acid; hence by diluting x Cc. to 1000 Cc. with water, the acid and alkali will react in equal volumes.

Having measured off x Cc. of the alkali, diluted to one liter, and mixed well, we repeat the titration of 50 Cc. to ascertain the exact content of alkali. Let there be required V' Cc. of the acid; then if one Cc. of the acid contains a gram of H_2SO_4, the weight of H_2SO_4 neutralizing the alkali in 50 Cc. of the caustic solution is $a.\ V'$. Hence the proportion

$$2KOH\ (112.236) : : H_2SO_4\ (98.086) : : Y : a\ V'.$$

And $\frac{Y}{50}$ is the weight of potassium hydrate in one Cc. of the caustic solution determined by the aid of phenol-phthalein as indicator.

* Analyst, 1894—100.

Example. 100 grams of 'potash by alcohol' was dissolved to one liter: 50 Cc. required 65.1 Cc. of standard acid of which one Cc. contained .05126 gram of H_2SO_4. Therefore $x = 768$ Cc.: and this volume diluted to one liter formed an approximately normal solution. Fifty Cc. was titrated and required 49.9 Cc. of acid, hence, $\frac{Y}{50} = .05854$, the weight of KOH in one Cc.

EXERCISE 8—A. ACIDITY OF VINEGAR.

"Vinegar is a more or less colored liquid consisting essentially of impure dilute acetic acid, obtained by the oxidation of wine, beer, cider, or other alcoholic liquor." Wine vinegar has a specific gravity of 1.014 to 1.022, while that from malt is 1.017 to 1.019. Vinegar contains usually from three to six per cent of free acetic acid by weight; in some States the legal minimum is four per cent. It is frequently fortified by sulfuric or acetic acid,* rarely by hydrochloric.

On titration by standard alkali the free acid or acids are neutralized—$HC_2H_3O_2$ (acetic acid) $+ KOH = KC_2H_3O_2$ (potassium acetate) $+ H_2O$. From the volume of alkali solution may be calculated the percentage of free acid, assumed to be acetic.

From a pipette add 50 Cc. of vinegar to 100 Cc. or more of cold water containing a few drops of phenol-phthalein solution, and titrate to faint redness by standard potassium hydrate.

Calculation. Assuming the acid to be acetic,
$HC_2H_3O_2$ (60.032) : KOH (56.118) : : weight of $HC_2H_3O_2$: weight of KOH; and weight of $HC_2H_3O_2 \times 100 \div 50 =$ per cent of acetic acid by weight in one volume of vinegar.

Example. Required for 50 Cc. of vinegar 41.1 Cc. of potassium hydrate solution containing .05854 gram of KOH per Cc. The percentage of acetic acid is therefore 5.14.

B. FREE ACIDS IN CITRUS FRUITS.

The grateful acid taste of fruits of the citrine genus is due to free organic acids mostly citric; in lemon pulp it averages from eight to ten per cent.†

Strain the pulp of a large lemon through brass wire gauze to remove seeds and fiber. Weigh a small beaker, introduce about 25 grams of the juice, and again weigh. Rinse with cold water into a large beaker and titrate by standard potassium hydrate and phenol-phthalein.

Calculation.

$$\underset{\text{Citric acid.}}{H_3C_6H_5O_7\ (192.064)} + 3KOH\ (168.354) = \underset{\text{Potassium citrate.}}{3K_3C_6H_5O_7} + 3H_2O.$$

EXERCISE 9—CHLORAL HYDRATE.

Chloral (C_2HCl_3O) is an oily colorless liquid of a pungent odor. It is formed on passing dry chlorine into absolute alcohol for a long time, the principal reaction being $C_2H_5OH + 4Cl_2 = C_2HCl_3O + 5HCl$. However, by a secondary reaction between the alcohol and hydrochloric acid there is formed water—$C_2H_5OH + HCl = (C_2H_5)Cl + H_2O$—which immediately unites with the chloral to form chloral hydrate, so that chloral itself is not obtained by this process.

Chloral hydrate, $CCl_3.CH(OH)_2$, is a colorless compound crystallizing in the

* Analyst, 1893—180 and 1894—89.
† Journ. Chem. Socy. 28—937.

monoclinic system, melting at 57° and boiling at 97.5°. It is soluble in water alcohol and ether. As found in pharmacy in the form of clusters of small crystals or crusts, it is usually quite pure, though occasionally containing a small amount of free organic acid. Employed in medicine as a sedative, its action on the human economy is said to depend on its decomposition into chloroform. It is deliquescent, has a faint odor, and may be sublimed without decomposition.

When an aqueous solution of chloral hydrate is mixed with a caustic alkali it is decomposed into chloroform, an alkali formate, and water, the mixture becoming turbid from the separation of minute globules of the chloroform —

$$CCl_3.CH(OH)_2\ (165.374) + KOH\ (56.118) = CHCl_3 + KCHO_2 + H_2O.$$

A determination may be made by dissolving a weighed quantity of the hydrate in water, decomposing it by an excess of standard potassium hydrate, and titrating the excess of alkali by standard acid.

Dissolve a few grams of the commercial medicinal chloral hydrate in water and test the reaction with blue litmus paper.

Weigh quickly (to avoid absorption of moisture from the air) about five grams, brush into a 12-ounce beaker, and dissolve imabout 150 Cc. of cold water. Should the above test show the presence of free acid, stir in a little precipitated calcium carbonate, filter and wash with cold water. Add from a pipette 50 Cc. of standard potassium hydrate, stir well, and titrate by standard sulfuric acid and phenol-phthalein. Also titrate 50 Cc. of the alkali by the acid.

Calculation. In the above equation 56.118 parts of potassium hydrate decompose 165.374 parts of chloral hydrate, or one gram decomposes $\frac{165.374}{56.118} = 2.947$ grams.

Let a be the volume of sulfuric acid neutralizing 50 Cc. of the alkali, and b the volume of sulfuric acid required in the residual titration; then $a-b$ is the volume of acid equivalent to the alkali decomposing the chloral hydrate.

Let c be the weight of potassium hydrate neutralized by one Cc. of the acid, then $(a-b) \times c$ is the weight of potassium hydrate required to decompose the chloral hydrate; and since one gram of potassium hydrate decomposes 2.947 grams of chloral hydrate, then

$(a-b) \times c \times 2.947$ is the weight, and

$(a-b) \times c \times 2.947 \times \frac{100}{\text{weight of sample}}$ is the percentage of chloral hydrate in the sample.*

Example. Fifty Cc. of the potassium hydrate solution required 49.3 Cc. of the sulfuric acid for neutralization. One Cc. of the acid neutralized .057119 gram of KOH.

Weight of sample.	Residual titration.	Percentage of chloral hydrate.
5.146 grams.	19.4 Cc.	97.82
5.008 "	20.1 "	98.25
5.237 "	18.8 "	98.03

* Allen, Coml. Org. Anal. 1—239.

EXERCISE 10—ACETIC ACID.

Determination of the Rate of Distillation from an Aqueous Solution.

When a dilute solution of acetic acid is fractionally distilled the acid accompanies the water, not uniformly, however, but in a constantly increasing ratio. That is, of a number of fractions of equal volume, each contains more acid than its predecessor. Richmond* states the following laws of the volatility of the higher fatty acids (page 320) from a dilute solution.

1. Each acid on distillation behaves as a perfect gas and conforms to Henry's law [that when equilibrium is established between a gas and a liquid in contact, the ratio of the concentration of the gas to that dissolved in the liquid is a constant for any given pressure].

2. Each acid has a fixed rate of distillation which is an inverse function of its solubility in water and is quite independent of the properties of the pure acids.

3. The apparent rate of distillation may be modified by condensation in the retort.

He proposes the following formula

$$(100-y)=\frac{(100-x)^a}{100^{a-1}}.\ K^{-x};\ \text{or}\ y=100-\frac{(100-x)^a}{100^{a-1}}.\ K^{-x}$$

in which x is any percentage of the total volume distilled; y, the corresponding percentage of the total acid distilled; and a, the ratio between the acid-content of the vapor and that of the liquid in the retort — for acetic acid it is about .667.

In distilling from an ordinary retort or flask more or less condensation of aqueous vapor takes place by contact with the upper air-cooled part of the distilling vessel, the drops formed running back into the liquid; the amount of this air-condensation depends on the extent of the surface of the unoccupied part of the still, the rapidity of boiling, temperature of the air, draughts, etc. A little consideration of Henry's law will show that the acid-content (concentration) of the air-condensed liquid is intermediate between those of the vapor and the liquid in the retort; and as in distilling dilute acetic acid the acidity of the vapor is always *less* than that of the liquid in the retort ($a=.667$), the air-condensed drops are always *stronger* in acid than the remaining vapor. Hence the greater the air-condensation the weaker will be the vapor as it enters the condenser, and, of course, the distillate as well. Obviously, therefore, if concordant results are to be expected in several distillations, either the operation must be conducted under rigidly uniform conditions, or a correction deduced and applied. Richmond (loc. cit) adopts an approximate correction expressed as a logarithmic function of the volume of the distillate, namely, K^{-x} (*supra*), K varying with the amount of air-condensation; in the original experiments of Duclaux† it is nearly unity.

A weak aqueous solution of acetic acid is prepared by diluting about 20 Cc. of the glacial acid to 500 Cc. Two portions of 110 Cc. each are withdrawn by pipettes, one into a beaker and titrated by potassium hydrate and phenol-phthalein,

* Analyst, 1895—195 *et seq.*

† Ann. Chim. Phys. 5—2—233.

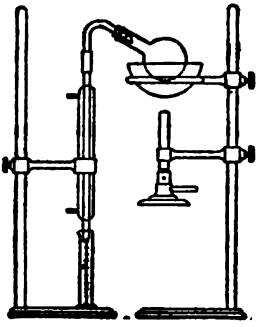

Fig. 138.

the other into a flask of about 250 Cc. capacity. Into the latter a few pieces of pumice-stone about the size of coffee-beans are thrown to secure regular boiling, and the flask is supported on a sand-bath and connected with a condenser by a rubber stopper, as shown in Fig. 138. Below the condenser is placed a 10 Cc. measuring jar for a receiver. After seeing that the stopper and connection with the condenser are steam-tight, the burner is lighted and the liquid gently boiled.

The distillation proceeds slowly, and when ten Cc. has come over another measuring jar is substituted for the first. The distillate is carefully poured into a large beaker and the jar rinsed by once filling with water and pouring into the beaker. After titration by standard alkali and phenol-phthalein, the jar is dried by a roll of filter paper and substituted for the second jar when that has received ten Cc. The second fraction is poured into the beaker containing the first distillate, the jar rinsed and the titration continued. Ten fractions in all are collected and titrated, leaving about ten Cc. remaining in the flask.

Calculation. The volume of alkali required for each fraction times 100 divided by the volume required for 110 Cc. of the acid gives the percentage of acid in each fraction.

The percentage of acid divided by that calculated from the formula $y = 100 - \frac{(100 - x)^a}{100\,(a-1)}$ gives a factor of correction for air-condensation which should be fairly constant for all the fractions of any one distillation provided the conditions were uniform throughout. The results may be plotted as in Fig. 171.

Example. In the following table x represents the percentages of the volumes of successive fractions of the total distillate on the basis of 110 Cc. equaling 100 per cent; column y the percentage of acid in each volume as calculated by the above formula; columns A, B, and C, the results of three experiments conducted as described above; and a, b, and c, the respective factors of correction, or the ratio of A, B, and C, to y.

x	y	A Cc.	A Per cent.	B Cc.	B Per cent.	C Cc.	C Per cent.	a	b	c
9.09	6.2	4.6	6.3	4.2	5.8	4.8	6.5	.98	1.07	.95
18.18	12.5	9.4	12.8	8.7	11.9	9.8	13.3	.98	1.05	.94
27.27	19.1	14.4	19.6	13.2	18.0	15.0	20.3	.97	1.06	.94
36.36	26.0	19.5	26.6	18.1	24.7	20.4	27.6	.98	1.05	.94
45.45	33.3	24.9	34.0	23.2	31.7	25.9	35.1	.98	1.05	.95
54.54	40.9	30.5	41.6	28.5	38.9	31.7	43.0	.98	1.05	.95
63.64	49.0	36.6	49.9	34.2	46.7	37.9	51.4	.98	1.05	.95
72.73	57.9	43.1	58.8	40.5	55.2	44.5	60.4	.98	1.05	.96
81.82	67.9	50.7	69.2	47.9	65.3	51.9	70.4	.98	1.04	.96
90.91	79.8	59.6	81.3	57.0	77.8	60.3	81.8	.98	1.03	.97

110 Cc. required of standard alkali, in A, 73.3 Cc.; in B, 73.3 Cc.; in C, 73.7 Cc.

The effect of air-condensation is plainly shown in B and C; in both the distillation was made from the same flask. In B the amount of air-condensation was considerable and the distillation correspondingly slow (129 minutes) and therefore the distillate weaker throughout than in y, while in C the flask was closely covered by a non-conductor of heat (sheet asbestos), hence the air-condensation was small, the distillation rapid (42 minutes), and the distillate stronger than in y.

EXERCISE 11—HYDRASTIS.

Determination of Berberine.

Hydrastis, the dried rhizome and roots of the *Hydrastis Canadensis* nat. ord. *Ranunculaceae* (U. S. Pharmacopoeia). It is extensively used as a medicine and dispensed by pharmacists in the form of a fine powder or its fluid extract.*

The drug contains at least three alkaloids constituting the active principle—*berberine, hydrastine,* and *canadine.* The first named, considered by some to be the most important medicinally, assays upward of four per cent in the commercial powder. It is a yellow or brown crystalline solid ($C_{20}H_{17}NO_4$), inodorous and of a bitter taste. Soluble in hot water and alcohol, and unites with acids to form crystalline salts.

Berberine hydrochloride ($C_{20}H_{17}NO_4HCl.4H_2O$) crystallizes in yellow prisms sparingly soluble in water (100 parts), cold alcohol, and dilute acids, and very slightly in a mixture of alcohol and ether.

The assay of the drug is made by extracting the alkaloids by hot alcohol; precipitating the berberine by hydrochloric acid and ether; drying the precipitate, when it loses its water of crystallization; and weighing as $C_{20}H_{17}NO_4HCl$.

Dry the powdered hydrastis at 100°, and weigh one portion of ten grams and transfer to an 8-oz. beaker with 50 Cc. of alcohol (95 per cent); cover with a watch-glass and heat on the water bath for a half hour, stirring now and then. Run through a 12.5 Cm. filter into a 100 Cc. measuring flask; without washing, drop back the residue into the beaker, add 50 Cc. more alcohol, and heat again for a half hour. Filter through the same paper, and wash with hot alcohol until the mark on the flask is reached. After cooling, make up to exactly 100 Cc. with alcohol and mix well.

Draw out three lots of 25 Cc. into four-ounce Erlenmyer flasks. Add to each, one Cc. of concentrated hydrochloric acid, three drops of concentrated sulfuric acid, and 15 Cc. of ether. Close the flasks by smooth corks (not rubber stoppers), and shake the flasks until crystals appear. Let stand over night in a cool place.

Filter each on a smooth 9-Cm. paper and wash a few times with a mixture of equal volumes of alcohol and ether. A yellow coloring extract stains the filter and cannot be washed away without dissolving some of the precipitate—its weight is inconsiderable. Dry the filter first on blotting paper, then in the air-bath at 110° to 115° for an hour. Open the filter and transfer the precipitate to a tared watch-glass with the aid of a camels-hair brush and weigh.

Calculation. $C_{20}H_{17}NO_4HCl : C_{20}H_{17}NO_4 :: 371.634 : 335.176$.

Example. One gram of the dried powder treated as above gave .0740, .0735, and .0725 grams of the anhydrous hydrochloride, equivalent to 2.67, 2.65, and 2.62 per cent of the alkaloid in the drug.

EXERCISE 12—GUARANA.

Determination of Caffeine.

The guarana (*Paullinia Cupana* nat. ord. *Sapindaceae*) is a climbing shrub indigenous to Brazil. The seeds are dried and powdered, moistened with

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* Proc. Michigan Pharm. Assn. 1893; Prescott, Organic Anal. 71; Lloyd, Drugs and Medicines of N. A. 76; Amer. Journ. Pharm. 71—257; Journ. Amer. Chem. Socy. 1899—732.

water, and kneaded to a stiff paste which is dried, formed into rolls, and exported. The commercial article contains starch, gum, a green-colored fat, tannin, and from two to four per cent of the active principle the alkaloid caffeine (guaranine). The official medicinal fluid extract is a clear liquid of a deep red-brown color, peculiar odor, and astringent taste; it is made by the process of cold repercolation of the powdered guarana by diluted alcohol, the percolate being diluted until one cubic centimeter represents one gram of the drug and contains from 30 to 40 milligrams of caffeine in a menstruum of about three parts of alcohol to one part of water. It may be found at any pharmacy.

The assay of the fluid extract is made by diluting it with a magma of magnesium carbonate in water, thus neutralizing it and precipitating resin and various extractives. After filtering, the caffeine is absorbed or "shaken out" by chloroform from an aliquot part of the filtrate. On evaporation of the chloroform the anhydrous alkaloid is left nearly pure. Obtained in this way, caffeine ($C_8H_{10}N_4O_2$) is a crystalline mass of stellate tufts of colorless needles, permanent in the air, but subliming a little above 100°, and soluble in about 80 parts of water, 7 of chloroform, and 33 of alcohol. It may be identified by the 'murexoin reaction.'*

Into a 100 Cc. measuring-flask is introduced 10 Cc. of the fluid extract, allowing the pipette to drain for two minutes; this is diluted with about 80 Cc. of cold water, and about a gram of finely powdered commercial magnesium carbonate added. The mixture is shaken, made up to the mark with water, and well mixed. The precipitate and the excess of the carbonate are separated by filtration through a dry 11 Cm. paper into a dry beaker.

Two portions of the filtrate of 40 Cc. each are accurately measured from a tall measuring-jar or burette, and each extracted as follows: after pouring into a 50 Cc. burette with glass stopcock (or a small separatory funnel), 10 Cc. of chloroform is added, the burette stopped by the thumb and shaken vigorously to emulsify the liquids; then fixed in its stand, and the chloroform allowed to segregate below the aqueous stratum.

A glass dish (page 60), about three inches in diameter is weighed and nearly all the chloroform, containing a large proportion of the alkaloid, drawn into it, being careful not to allow any water or mucilaginous matter at their junction to follow. To withdraw what alkaloid remains, the aqueous solution is again shaken out with four successive portions of chloroform of 5 Cc. each.

The 30 Cc. of chloroform in the dish is now evaporated to dryness on the water bath at a heat insufficient to boil it. The dish is wiped dry and weighed after standing in the balance case for 15 minutes. The caffeine should be white or nearly so and distinctly crystalline; it is often fragrant, especially on heating, though the pure alkaloid is odorless.

Calculation. The volume of the magnesium carbonate and the precipitate it forms is not considered, as the error introduced is less than those from other sources. Since the alkaloid is obtained from $\frac{40}{100}$ of 10 Cc. (or 4 Cc.) of fluid extract, its weight times $\frac{100}{4}$ is the percentage W/V of caffeine in the extract.†

Example. Ten Cc. treated as above gave .153 and .152 gram of caffeine, equal to 3.82 and 3.80 per cent of the alkaloid in one volume of the fluid extract.

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* Prescott, Organic Anal. 79.

† U. S. Dispensatory, *Guarana*. Journ. Amer. Chem. Socy. 1896—978.

EXERCISE 13 — POTASSIUM PERMANGANATE.

Preparation of a Standard Solution.

The formula of this compound may be expressed as $K_2O.2MnO.O_5$. When brought in an acid solution in contact with a reducing agent the acid is decomposed, the hydrogen uniting with the five atoms of available oxygen to form water, while the potassium and manganese unite with the halogen or acid-rest to form proto-salts; thus, with nitric acid and hydrogen peroxide —

$$K_2O.2MnO.O_5 + 6HNO_3 + 5H_2O_2 = 2KNO_3 + 2Mn(NO_3)_2 + 5O_2 + 8H_2O.$$

The purple color of permanganic acid, perceptible in even extremely dilute solutions, is a well marked indication of the least excess, the proto-salts of potassium and manganese being colorless.

No great amount of hydrochloric acid may be present in the sulfuric or nitric solution of the compound to be titrated, especially if it be hot, lest the permanganate react with it also; *e. g.*, $K_2O.2MnO.O_5 + 16HCl = 2KCl + 2MnCl_2 + 5Cl_2 + 6H_2O$.

Four grams of the clean crystals is dissolved in a liter of pure water; after standing several hours the solution is decanted from any sediment. The solution slowly decomposes with age and immediately with most organic matter. The strength is ascertained before each series of analyses by titrating a known weight of an oxidizable salt, such as ferrous iron in a strongly acid solution —

$$10FeSO_4 + K_2Mn_2O_8 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + MnSO_4 + 8H_2O,$$

and is generally expressed as the weight of metallic iron oxidized by one cubic centimeter of the permanganate solution.

Weigh accurately about five grams of bright iron wire (page 209) and transfer to a one-liter measuring flask; add about 300 Cc. of water and 50 Cc of concentrated sulfuric acid, cover the flask with a watch-glass and heat gently until the iron is dissolved. Cool, add a few grains of metallic zinc (to reduce any ferric sulfate formed by oxidation), and when the zinc is dissolved, dilute to the mark with water and mix well. The solution slowly oxidizes on keeping.

Fill a burette with the permanganate solution, pipette 50 Cc. of the ferrous solution to a large beaker containing about 200 Cc. of cold water, and titrate to faint redness with constant stirring. The color persists for a few minutes only, the slight excess of permanganic acid reacting with the manganous salt present.

Calculation. The weight in grams of iron in 50 Cc. of the ferrous solution divided by the volume of permanganate solution used equals the weight in grams of iron oxidized by one cubic centimeter of the permanganate.

Example. Iron wire weighed 5.013 grams. Deducting .005 gram for impurities leaves 5.008. For 50 Cc. was required 35.5, 35.5 and 35.6 Cc. of permanganate; therefore one Cc. oxidizes .007053 gram of iron.

EXERCISE 14 — A. POTASSIUM CHLORATE.

Determination of Oxygen.

The salt crystallizes in colorless monoclinic plates soluble in 16 parts of cold and 2 parts of hot water. The most common impurity is potassium chloride, removable by recrystallization from hot water.

The determination is made by a residual titration. Sulfuric acid is decomposed on heating with a ferrous salt and a chlorate —

$$KClO_3 + 4H_2SO_4 + 6FeSO_4 = KHSO_4 + 3Fe_2(SO_4)_3 + HCl + 3H_2O.$$

If a known weight (an excess) of ferrous sulfate be dissolved, and what remains unoxidized be titrated by potassium permanganate, the weight of oxygen can be calculated.

Powder pure potassium chlorate, weigh one gram, and dissolve in exactly 500 Cc. of cold water in a half-liter measuring flask. Draw out with the pipette three portions of 50 Cc. into pint Erlenmyer flasks and add to each exactly 100 Cc. of the ferrous solution (page 209), and about 75 Cc. of dilute sulfuric acid (one acid to ten water). Cover the flasks by watch-glasses and heat to about 60° to 70° (not higher, lest the free hydrochloric acid act on the ferrous sulfate); then cool the flasks in a stream of water, dilute with 100 Cc. of cold water, and titrate by standard permanganate.

Calculation. From the above equation, three atoms of oxygen (48) react with six atoms of iron (336); hence the weight of iron in 100 Cc. of the ferrous solution, less that oxidized by the permanganate, multiplied by $\frac{48}{336}$ or $\frac{1}{7}$ is the weight of oxygen in .1 gram of the chlorate.

Example. Ferrous solution, 5.008 grams of iron wire in one liter. Permanganate, 4 grams per liter. Fifty Cc. of the former was oxidized by 35.5 Cc. of the latter, hence one Cc. of permanganate oxidized .007053 gram of iron. In the determination were required 32.1, 32.1, and 32.2 Cc. of permanganate, giving respectively 39.20, 39.20, and 39.10 per cent of oxygen. Theory requires 39.16 per cent.

B. FORGE SCALE.

Determination of Iron.

The scales detached when hot iron is hammered are composed of a mixture of iron protoxide and sesquioxide, with small amounts of metallic iron, oxide of manganese, etc. The ratio of the protoxide to the sesquioxide is quite variable, though approaching the proto-sesquioxide, Fe_3O_4.

As the scale is but slowly acted on by sulfuric acid, and a hydrochloric solution is inadmissible in a titration by permanganate, the solution is made first in the latter and this evaporated with an excess of the former, leaving a residue of ferric and ferrous sulfates soluble in hot water.

The iron is determined by finding the volume of standard permanganate required to convert it from the ferrous to the ferric state, so that previous to the titration, ferric sulfate must be reduced to ferrous by some reagent whose excess (used to insure complete reduction) can be easily removed or so altered as not to affect permanganate. Metallic zinc answers this requirement, as zinc sulfate does not react with permanganate and the excess of zinc may be decanted or filtered off or allowed to dissolve. The reaction involved in the reduction is $Zn + H_2SO_4 = ZnSO_4 + 2H$; and $Fe_2(SO_4)_3 + 2H$ (nascent) $= 2FeSO_4 + H_2SO_4$.

Grind a few grams of the clean scale to an impalpable powder in an agate mortar and dry at 100°. Weigh about one-half gram into a No. 2 beaker, add 20 Cc. of concentrated hydrochloric acid, stir well and digest in a warm place until all or nearly all seems to be dissolved. Slowly heat to near boiling, add-

ing a crystal of potassium chlorate to destroy any carbonaceous matter originally present as carbon in the iron.

Dilute the solution with 50 Cc. of hot water and filter through a small paper into a 20-oz. beaker; wash the filter alternately with hot water and dilute hydrochloric acid until no ferric chloride remains in the paper. Add to the filtrate about 5 Cc. of concentrated sulfuric acid and evaporate on the hot plate until white fumes of sulfuric acid appear.

Dissolve the ferric sulfate in a little hot water, dilute with 200 Cc. of cold water, and drop in about 5 grams of granulated or powdered zinc. When the solution has become colorless, add more sulfuric acid to complete the solution of the zinc, and test a drop of the liquid by potassium sulfocyanide — only a faint red color should appear. When all the zinc has dissolved, the watch-glass is rinsed and the solution immediately titrated by standard permanganate.

Zinc usually contains carbon and iron in quantities that will reduce a perceptible volume of permanganate, and for a correction five grams is dissolved in dilute sulfuric acid and the solution titrated, the volume of permanganate used to be deducted from the former reading.

Calculation. Let the volume of the permanganate used be V; the volume used for the blank titration of five grams of zinc be v; the weight of iron oxidized by one Cc. of the permanganate be F; and the weight of scale taken for analysis be W; then $(V - v) \times F \times \frac{100}{W}$ is the percentage of metallic iron in the scale.

Example. A weight of .496 gram of scale treated as above required 51.0 Cc. of permanganate, of which one Cc. oxidized .007053 gram of iron. Deducting .1 Cc., the volume required for five grams of zinc, the percentage of iron in the scale was 72.38.

If there were contained in the scale only ferrous and ferric oxides the proportion of each could be calculated according to the formula

$$\left(\frac{\text{Percentage of iron} \times 160}{112} - 100\right) \times \frac{144}{16} = \text{percentage of FeO.}$$

Problem. Given a dry powder consisting of a mixture of Fe_3O_4 and Fe_2O_3, to determine by a chemical process the percentages of each without the use of the balance or standardized volumetric solutions.

EXERCISE 15 — CHROME YELLOW.

Determination of Lead Chromate.

The pigment known to the trade as chrome yellow, lemon chrome, etc., is essentially normal chromate of lead, $PbCrO_4$, and is sold as a fine powder or ground in oil. To produce the lighter shades a suitable proportion of a white pigment, such as barium sulfate, lead sulfate, china clay, etc., is admixed during the manufacture, so that the commercial pigment often contains less than half its weight of lead chromate.

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(1). On heating the powder with dilute sulfuric acid the lead chromate is decomposed with the formation of chromic acid and insoluble lead sulfate:

$$2PbCrO_4 + 2H_2SO_4 = 2H_2CrO_4 + 2PbSO_4 \quad \ldots\ldots (1)$$

any carbonates present are also converted into sulfates.

(2). Chromic acid reacts with a ferrous salt, in presence of a free mineral

acid, to form a chromous and a ferric salt; thus, with ferrous sulfate and sulfuric acid —

$$2H_2CrO_4 + 6FeSO_4 + 6H_2SO_4 = 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + 8H_2O \ldots\ldots\ldots\ldots (2)$$

(3). Ferric salts are not precipitated by a ferricyanide, while a ferrous salt produces a blue precipitate, or if very dilute, a blue coloration. Lead sulfate and insoluble matter do not interfere with this reaction.

The determination is done by digesting the pigment with sulfuric acid, when chromic acid is liberated according to equation (1). The chromic acid is then titrated by a standard solution of ferrous sulfate according to equation (2). The end-point is shown by ferricyanide. The solutions needed for the determination are the standard solution of ferrous sulfate, page 229, containing about .005 gram of iron per cubic centimeter, and one of potassium ferricyanide, page 209.

The finely powdered pigment is dried at 100°, and four portions of one gram each weighed and transferred to eight-ounce beakers. Into each is poured about 50 Cc. of cold water followed by five Cc. of concentrated sulfuric acid, and the mixture stirred until the yellow lead chromate has wholly passed to the white sulfate. The turbid yellow liquid is then diluted with about an equal volume of cold water and titrated by the ferrous solution.

The end-point is found by placing several separate drops of the ferricyanide solution on white drawing paper or a glazed white tile, and, after each addition of the titrand and *stirring well*, letting fall a drop of the titrate from a glass rod into one of the drops on the paper. When a distinct blue or greenish-blue color appears, the ferrous sulfate is in excess and the titration is finished.

The first titration is made by running in the titrand in volumes of five Cc. at a time, this showing the volume required to within that limit. To the second is added at once a volume less by five Cc. than that of the first titration, and concluded by additions of .2 Cc. The third and fourth may be treated at once by one Cc. less than the second titration, and finished by .1 Ccs.

A measurable volume of the ferrous solution is needed to produce a blue color with ferricyanide, and this volume should be deducted from every reading. It is found by titrating as above a mixture of 100 Cc. of water with 5 Cc. of sulfuric acid, but adding the titrand in drops only.

Calculation. From the equations under (1) and (2), we see that two molecules of lead chromate react with six molecules of ferrous sulfate or with six atoms of iron.

Let a be the weight of the sample of chrome yellow; b, the weight of iron in one Cc. of the ferrous solution; c, the weight of lead chromate reduced by one Cc. of the ferrous solution; d, the volume of ferrous solution used for the titration, and d', the volume used in the blank; and x, the percentage of lead chromate in the sample: then 336 (6Fe) : 646.04 ($2PbCrO_4$) : : b : c;

whence $c = \frac{646.04\ b}{336} = 1.9227\ b$. Then $x = c \times (d - d') \times \frac{100}{a}$.

Example.

	a	b	c	d	d'	x
A.	1.000	.005006	.009623	25 — 30	.4	.....
B.	"	"	"	28.8	"	27.33
C.	"	"	"	28.5	"	27.04
D.	"	"	"	28.7	"	27.23

EXERCISE 16—METOL.

Determination of Sulfuric Acid.

Metol is the trade-name of an organic compound largely used as a photographic developer. Chemically it is a phenol derivative, the sulfate of monomethyl-paraamidophenol, $CH_3.NH.C_6H_4OH.\frac{H_2SO_4}{2}$ (172.155). It is found in the market in the form of minute colorless needles, very soluble in water, and slightly soluble in alcohol and ether. The aqueous solution darkens on standing through oxidation by the air.

On treating an aqueous solution of metol with barium chloride the sulfuric acid is precipitated as barium sulfate, leaving the chloride of monomethyl-paraamidophenol in solution—

$$2\left(CH_3.NH.C_6H_4OH.\frac{H_2SO_4}{2}\right) + BaCl_2 = 2\left(CH_3.NH.C_6H_4OH.HCl\right) + BaSO_4.$$

Barium sulfate is a white powder, infusible at a white heat, insoluble in water, and but slightly soluble in dilute hydrochloric acid. It is unaltered on ignition, though a small amount may be reduced to barium sulfide when heated with carbon.

A weighed quantity of metol is dissolved in water, acidulated by hydrochloric acid, and precipitated by barium chloride. The liquid is filtered and the barium sulfate washed with hot water, ignited and weighed. From the weight is calculated the proportion of sulfuric acid in the metol.

Weigh accurately three portions of metol of about three grams, and transfer to 12-ounce Griffen beakers. Dissolve each in about 200 Cc. of hot water and acidify by ten Cc. of concentrated hydrochloric acid. Precipitate by a small excess of barium chloride solution, stir well, and let stand until the supernatant liquid is clear. Filter through a close double 9-Cm. paper (or one of Dreverhoff's No. 400), and wash thoroughly with hot water.

Weigh a clean platinum crucible, fold the filter paper around the precipitate, and put into the crucible. Wipe off any barium sulfate adhering to the funnel by a small piece of filter paper. Heat the crucible gently until no more smoke appears, incline the crucible as in Fig. 94, and burn the charred paper at a low heat. Cover the crucible, heat to redness for a few minutes, cool and weigh.

Put a few drops of water in the crucible and one drop of dilute sulfuric acid, this to convert any barium sulfide to sulfate. Evaporate the water on the water bath, and gently ignite the covered crucible, finally to redness. Cool and reweigh.

Calculation. Weight $BaSO_4$: weight H_2SO_4 : : 233.47 : 98.086.

Hence, Weight $BaSO_4 \times \frac{98.086}{233.47} \times \frac{100}{\text{Weight of metol}}$ = per cent of sulfuric acid in metol.

Example. Sample of Hauff's manufacture.

	A.	B.	C.
Weight of metol	3.025	3.264	3.538 grams.
Weight of barium sulfate	2.056	2.219	2.408 grams.
Percentage of sulfuric acid	28.55	28.56	28.60
Theoretical percentage	28.49		

EXERCISE 17 — A. SODIUM THIOSULFATE.

Sodium thiosulfate, $Na_2S_2O_3.5H_2O$ (formerly called sodium hyposulfite) crystallizes in clear colorless prisms slowly efflorescing in the air. Like many other commercial salts, the article sold as "commercially pure" contains but little impurity. The most common impurities are other sodium salts, sometimes calcium sulfate. It may be purified by recrystallization from hot water.

The crystals dissolve in about an equal weight of cold water. On acidifying an aqueous solution by a mineral acid, thiosulfuric acid is set free — $Na_2S_2O_3 + H_2SO_4 = Na_2SO_4 + H_2S_2O_3$. But after a short time the thiosulfuric acid spontaneously decomposes into sulfurous acid and free sulfur — $H_2S_2O_3 = H_2SO_3 + S$ — the separated sulfur making the liquid milky white. The more concentrated and warmer the solution, the more quickly does the decomposition set in.

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1. Potassium permanganate reacts with potassium iodide in an acid solution, liberating iodine —

$$10KI + K_2Mn_2O_8 + 8H_2SO_4 = 5I_2 + 6K_2SO_4 + 2MnSO_4 + 8H_2O.$$

2. Free iodine reacts with sodium thiosulfate to form sodium tetrathionate —

$$2Na_2S_2O_3.5H_2O + I_2 = Na_2S_4O_6 + 2NaI + 5H_2O.$$

3. In an acid solution, free iodine combines with dissolved starch to form the intensely blue starch iodide; this compound is decomposed by thiosulfuric acid.

For the determination a weighed amount of the crystals is dissolved in water, an excess of potassium iodide and a little starch-paste are added, and the solution acidified by sulfuric acid. Standard permanganate is run in from a burette; as it enters the titrate the reaction (1) above takes place, then the liberated iodine immediately reacts with the thiosulfate as in equation (2); finally, when all of the thiosulfate has passed to tetrathionate, the least excess of free iodine unites with starch and the solution becomes permanently blue, showing the end-point.

Four solutions are used in the determination.

1. Potassium permanganate of a concentration of about four grams per liter, prepared and standardized as described on page 229.

2. Potassium iodide, made by dissolving about 20 grams of the compound in 100 Cc. of water.

3. Starch-paste, made by stirring up about one-half a gram of starch powder in a little cold water and pouring into 100 Cc. of boiling water.

4. Dilute sulfuric acid — about one volume concentrated acid to two volumes of water.

A weight of about ten grams of the crystallized thiosulfate is dissolved in cold water in a 500 Cc. measuring flask and the solution made up to the mark.

Preliminary titration. Into a large beaker is poured about 300 Cc. of cold water, 20 Cc. of the potassium iodide solution, a few Cc. of the starch-paste, and one Cc. of dilute sulfuric acid. The beaker is placed under a burette filled with permanganate, 50 Cc. of the thiosulfate solution run in from a pipette, and the liquid immediately titrated until blue.

The volume of permanganate used in this titration will be a few cubic centimeters greater than corresponds to the equations, due principally to the

decomposition of a part of the thiosulfuric acid as before mentioned (one molecule of sulfurous acid is oxidized to sulfuric acid by *two* molecules of iodine). To eliminate this error, the titration is repeated with the modification of adding the thiosulfate to a solution containing a quantity of free iodine nearly sufficient for its entire conversion to tetrathionate.

Titration. A large beaker is charged with about 300 Cc. of cold water, 20 Cc. of the potassium iodide solution, a few Ccs. of starch-paste, and one Cc. of dilute sulfuric acid. Into this is run from the burette a volume of permanganate less by three or four Cc. than that used in the preliminary titration. Then 50 Cc. of the thiosulfate solution is run in from a pipette with constant stirring, and the titration immediately continued to the end point.

Calculation 1. From the equation (4) below, we see that one molecule of permanganate oxidizes ten atoms of iron from the ferrous to the ferric state. From the equation (1) above, we see that one molecule of permanganate liberates ten atoms of iodine from potassium iodide. The atomic weights of iron being 56, and of iodine, 126.85, it follows that one Cc. of permanganate solution will oxidize iron and set free iodine in the ratio of 10×56 to 10×126.85; that is, if one Cc. of permanganate solution oxidizes a grams of iron, it will liberate $\frac{1268.5a}{560}$ grams of iodine.

2. From equation (2), we note that one atom of iodine (126.85) reacts with one molecule (248.32) of crystallized sodium thiosulfate. Hence the weight of iodine used in the reaction times $\frac{248.32}{126.85}$ will equal the weight of thiosulfate.

3. Combining the above, $\frac{1268.5\,a}{560} \times \frac{248.32}{126.85} \times$ volume of permanganate solution used equals the weight of thiosulfate.

4. If V represents the volume of permanganate used in the titration; W, the weight of the thiosulfate; and a, the weight of iron oxidized by one Cc. of the permanganate solution; then the percentage of crystallized sodium thiosulfate in the sample is $4.4344\ a.\ V.\ \frac{100}{W}$

Example. A commercial article of fair quality. Weight of thiosulfate 10.361 grams. One Cc. of permanganate oxidized .007049 gram of iron.

Preliminary titration.....	33.8 Cc.	= 101.98	per cent.
First titration.....	30.0 + 2.7 Cc.	= 98.66	"
Second "	31.0 + 1.7 Cc.	= 98.66	"
Third "	32.0 + .6 Cc.	= 98.36	"

B. MANGANESE IN STEEL.

All varieties of steel contain a small proportion of manganese which is incorporated during the manufacture for the purpose of counteracting the effect on the strength and ductility of the metal of the various impurities unavoidably present. The proportion ranges from .1 to over one per cent, depending on the character of the steel and the use for which it is intended.

1. When heated with moderately dilute nitric acid steel dissolves completely, the iron and manganese becoming respectively ferric and manganous nitrates, while the carbon is converted to a hydrated compound passing completely into solution with a brown color.

2. If from this solution the water be evaporated, the residue mixed with hot

concentrated nitric acid, and crystals of potassium chlorate added, first the carbon is oxidized to carbon dioxide, then the manganese precipitated as binoxide; *e. g.* —

$5Mn(NO_3)_2 + 2KClO_3 + 4H_2O = 5MnO_2 + 2KNO_3 + 8HNO_3 + 2Cl$ ..... (1).

in the form of a fine black powder; the iron remains almost entirely in solution.

3. In a dilute acid solution hydrogen peroxide dissolves manganese binoxide to a manganous salt with evolution of oxygen, both compounds yielding an atom of oxygen to form a molecule —

$MnO_2 + H_2O_2 + 2HNO_3 = Mn(NO_3)_2 + 2H_2O + O_2$ ..... (2).

4. Hydrogen peroxide reacts with potassium permanganate in a similar manner —

$K_2Mn_2O_8 + 5H_2O_2 + 6HNO_3 = 2KNO_3 + 2Mn(NO_3)_2 + 8H_2O + 5O_2$ ..... (3).

5. The reaction between ferrous sulfate and permanganate is

$K_2Mn_2O_8 + 10FeSO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$ .... (4).

The determination is made by dissolving a weighed amount of steel in dilute nitric acid, concentrating the solution, compounding with concentrated nitric acid, and precipitating the manganese by potassium chlorate. The (unfiltered) solution is diluted with water and the precipitate dissolved by a known volume of standard solution of hydrogen peroxide. The excess of the hydrogen peroxide is titrated back by standard permanganate, and the percentage of manganese in the steel calculated from the volume required.*

Three standard solutions are required —

Potassium permanganate. Made by dissolving .8 gram in one-half liter of water; or by mixing 200 Cc. of the standard solution, page 229, with 300 Cc. of water. The solution is standardized by titrating 50 Cc. of the ferrous solution following.

Ferrous sulfate. Made by dissolving about .500 gram of iron wire in dilute sulfuric acid and diluting to 250 Cc. with cold water.

Hydrogen peroxide. The commercial medicinal 'ten-volume' article is assayed and diluted to a convenient strength. Exactly two cubic centimeters is run into about 200 Cc. of water, ten Cc. of dilute sulfuric acid added, and titrated by the permanganate solution. The quotient of 700 divided by the volume of permanganate solution required is the number of cubic centimeters of the hydrogen peroxide to be diluted with water, plus a little sulfuric acid, to 500 Cc. This solution slowly decomposes on keeping.

The steel for the analysis may be drillings or chippings of a Bessemer steel rail, perfectly free from dirt, oil or rust. The percentage of manganese contained will probably be between .75 and 1.25. Three portions of about two grams each are weighed and transferred to eight-ounce Griffen beakers, and each dissolved in a mixture of 20 Cc. concentrated nitric acid with 25 Cc. of water. When action ceases, the solution is boiled for a few minutes, then evaporated until a thick scum forms on the surface. The residue is taken up in 25 Cc. of concentrated nitric acid, and the beaker, covered with a watch-glass, is heated to boiling on a hot plate. While briskly boiling, a crystal of potassium chlorate (say .1 gram) is thrown in; yellow fumes appear, which may suddenly vanish after a short time; if not, a small crystal is added to the

* Journ. Socy. Chem. Ind. 1898—185.

boiling solution every few minutes until this occurs. Finally another crystal is added and the solution boiled for a few minutes longer, then set aside to cool.

Cold water is poured in until the beaker is half filled, then 50 Cc. of the hydrogen peroxide solution run in from a pipette. After stirring until clear, the liquid is immediately titrated by permanganate to a faint pink — the color fades rapidly.

The relation of the permanganate to the peroxide solution is found by diluting 50 Cc. of the latter with 200 Cc. of water, adding 25 Cc. of concentrated colorless nitric acid and titrating by the former. A reaction lag may often be observed at the beginning of the titration, but after a trace of manganous nitrate is formed the reaction proceeds regularly.

Calculation. Let a be the weight of iron oxidized by one Cc. of the standard permanganate; b, the weight of steel; c, the volume of permanganate reducing 50 Cc. of the peroxide solution; d, the volume of permanganate used in the titration; and X, the percentage of manganese in the steel.

1. The difference between the volumes of permanganate solution required for 50 Cc. of the peroxide and for the titration, $(c - d)$, is the volume equal in oxidizing power to the precipitate of MnO_2.

2. From equations (3) and (4) we see that $K_2Mn_2O_8$ (316.22) oxidizes 10Fe (560), and likewise $5H_2O_2$ (170.08). Hence, if one Cc. of permanganate solution oxidizes a grams of iron, it will also oxidize $\frac{170.08}{560}\ a$ or $.3037\ a$ grams of hydrogen peroxide.

3. From equation (2), one molecule of MnO_2, containing one atom of manganese (55), is reduced by one molecule of H_2O_2 (34.016). Hence one gram of H_2O_2 corresponds to $\frac{55}{34.016} = 1.6169$ grams of Mn; and one Cc. of permanganate solution corresponds to $.3037\ a \times 1.6169 = .491\ a$ grams of Mn.

4. The volume of permanganate solution $c - d$ is that volume which would reduce the same weight of H_2O_2 as does the MnO_2. Hence $(c - d)\ .491\ a$ is the weight of manganese in the sample of steel dissolved for analysis.

5. Since b is the weight in grams of the steel, $\frac{(c - d)\ .491\ a}{b} \times 100 = X$, the percentage of manganese in the steel. More conveniently the formula is expressed as $49.1\ a = F$, and $X = \frac{F(c - d)}{b}$

Example. Drillings of rail-steel. Permanganate solution, .8 gram in 500 Cc. of water. Ferrous solution, .5100 gram of iron in 250 Cc. of dilute sulfuric acid. Titration of 50 Cc. of the ferrous solution required 36.1 Cc. of permanganate; hence one Cc. of permanganate oxidizes .002825 gram of iron. Of the hydrogen peroxide solution, 50 Cc. was reduced by 35.4 Cc. of permanganate.

	a	b	c	d	F	X
A.	.002825	2.023	35.4	18.6	.1386	1.15
B.	"	2.014	"	19.1	"	1.12
C.	"	2.009	"	18.9	"	1.14

EXERCISE 18 — GALENA.

Determination of Lead.

The mineral is a sulfide of lead, formula PbS, crystallizing in the isometric system with an eminent cubic cleavage.

1. If the powder be treated with an excess of metallic zinc and a dilute acid a replacement occurs, the nascent hydrogen abstracting the sulfur;

$$PbS + Zn + 2HCl = Pb + ZnCl_2 + H_2S.$$

The lead remains as a dark coherent mass but slightly soluble in dilute hydrochloric acid, and completely insoluble during the evolution of hydrogen.

2. Metallic lead dissolves readily in *dilute* nitric acid leaving as a residue any quartz, etc., that may be present in the gangue.

3. If sulfuric acid be added to a solution of lead, a precipitate of lead sulfate will fall,

$$Pb(NO_3)_2 + H_2SO_4 = PbSO_4 + 2HNO_3.$$

It is a white powder soluble in 22800 parts of cold water, more readily in nitric acid, and less so in alcohol and dilute sulfuric acid. The presence of salts of zinc does not interfere. On ignition it is unchanged, except when in contact with reducing agents which convert it to metallic lead.

Select pure cleavage cubes and grind to a fine powder in an agate mortar. Weigh about two grams and brush into a tall beaker. Add 150 Cc. of cold water, about four grams of powdered or granulated zinc, and 20 Cc. of hydrochloric acid. Cover with a watch-glass and let stand until the liquid has become clear and no longer smells of hydrogen sulfide.

Dilute with an equal volume of water, stir and allow to settle. Decant carefully nearly all the solution from the lead and excess of zinc, and dissolve the metals by pouring in 100 Cc. of hot water and 15 Cc. of nitric acid. Pour the solution through a small filter and dissolve any lead sulfate in the residue of gangue with a little hot dilute hydrochloric acid, finally washing the filter with hot water.

Add to the filtrate 25 Cc. (an excess) of dilute sulfuric acid and evaporate on the water-bath until the nitric acid is entirely expelled, known by the absence of its odor. Cool the beaker and dilute the excess of sulfuric acid, now concentrated, with about 50 Cc. of cold water, stir well and filter through a 9 Cm. paper, washing with dilute alcohol (equal volumes of strong alcohol and water) until sulfuric acid is removed. Dry the filter at 100°.

Remove the precipitate from the paper and burn the latter in a weighed *porcelain* crucible. Moisten the ash with a few drops each of water and nitric acid, and one drop of dilute sulfuric acid. Evaporate to dryness and heat until the excess of acid is driven off. Introduce the lead sulfate, heat gently and weigh.*

Calculation. (1). $PbSO_4 : Pb :: 302.99 : 206.92$.
(2). Wt. of galena : wt. of lead :: 100 : per cent of lead.
(3). Theoretically, $PbS : Pb :: 238.99 : 206.92$.

Example. Two grams of galena gave 2.534 grams of $PbSO_4$, equal to 1.7305 grams of lead, equal to 86.53 per cent. Theory requires 86.59.

EXERCISE 19 — BARIUM CHLORIDE.

Complete Analysis.

The crystallized salt ($BaCl_2.2H_2O$) is purified as directed on page 207.

1. From the aqueous solution barium is precipitated by ammonium carbonate — $BaCl_2 + (NH_4)_2CO_3 = BaCO_3 + 2NH_4Cl$ — as white granular $BaCO_3$ soluble in acids and slightly so in water, but insoluble in neutral or alkaline solutions

* Crookes, Select Methods, 350; Fresenius Quant. Anal. 300.

of ammonium salts. It may be ignited alone without alteration, but is reduced to oxide by carbon; the oxide can be reconverted by heating with ammonium carbonate, ammonia being liberated.

2. If silver nitrate be added to a solution of a metallic chloride curdy white silver chloride is precipitated — $BaCl_2 + 2AgNO_3 = Ba(NO_3)_2 + 2AgCl$. Exposure of the precipitate to actinic light results in a superficial decomposition with the formation of silver subchloride, chlorine escaping, and loss of weight.

Silver chloride is insoluble in water and dilute acids, and may be heated to incipient fusion without change except in presence of carbon or reducing gases which transform it to metallic silver.

3. On heating crystallized barium chloride to redness the water is expelled; usually also a little chlorine is lost but can be restored by heating with ammonium chloride — *e. g.*, $BaO + 2NH_4Cl = BaCl_2 + 2NH_3 + H_2O$.

Barium. Weigh about one gram of the crystals into a 12-ounce beaker; dissolve in about 200 Cc. of hot water, and precipitate by an excess of solution of ammonium carbonate in dilute ammonia. Allow to settle until the supernatant fluid is clear, filter and wash with a dilute solution of the precipitant until no reaction for chlorine is found in the washings when tested with silver nitrate. Burn the filter and contents in a platinum crucible. Moisten the residue with a few drops of the reagent, dry, heat to dull redness and weigh.

Chlorine. Dissolve about one gram in a 12-ounce beaker in 300 Cc. of hot water; add, while stirring, a solution of silver nitrate until no further precipitation occurs, then about 5 Cc. of strong nitric acid and allow to settle. Filter and wash with hot water until silver is removed, breaking up the clumps of precipitate with a glass rod. Cover the funnel with a filter paper and dry in the water oven. All these operations are to be conducted with as little exposure to the light as possible.

Remove the precipitate as completely as can be done by shaking and rubbing the filter, fold the latter tightly and burn it in a small weighed porcelain crucible. Moisten the ash with a few drops of dilute nitric acid and heat for a moment, then with a drop of hydrochloric acid and evaporate to dryness on the water-bath; bring in the precipitate, heat till the edges begin to melt, and weigh as AgCl.

Water of crystallization. Heat one to three grams to dull redness in a platinum crucible for 15 minutes. Cool, add a few grains of pure ammonium chloride and heat gently until the excess is expelled. Cool and weigh; the loss is water.

Calculation.

Weight of $BaCO_3$	: weight of Ba	: : 197.40	: 137.40.
Weight of AgCl	: weight of Cl	: : 143.37	: 35.45.
Weight of $BaCl_2.2H_2O$	: weight of $2H_2O$	: : 100.00	: per cent of H_2O. *

Example.

.996 gram gave		.808 gram of $BaCO_3$		= 56.29	per cent	of Ba.
1.002	"	1.171	"	AgCl	= 28.90	"	" Cl.
2.671	"	.398	"	H_2O	= 14.90	"	" H_2O.

* Fresenius, Quant. Anal. 791. Chem. News, 1894—29 and 64. Crookes, Select Methods, 571.

EXERCISE 20 — LARD.

Pure lard is a mixture in somewhat variable proportions of tri-olein $C_3H_5(C_{18}H_{33}O_2)_3$, tri-stearin $C_3H_5(C_{18}H_{35}O_2)_3$, and tri-palmitin $C_3H_5(C_{16}H_{31}O_2)_3$. The commercial article is sometimes adulterated with water (up to 25 per cent or more), cotton-seed stearin or beef-tallow; a little salt may be legitimately incorporated to preserve it. Good lard is pure white in color, and nearly tasteless and odorless.

A. The water contained is determined by drying at a temperature somewhat above 100°, as at this temperature all the water may not be driven off.

B. The non-drying oils and fats on exposure to light and air acquire an acid reaction due to the conversion of a small portion of the glycerides into free fatty acids, and this change is accompanied to a certain extent by the alteration in odor and taste known as rancidity. In fresh lard the free acid should not exceed a small fraction of one per cent. As the change takes place more readily with olein than with stearin or palmitin, the free acid is generally expressed as so much oleic acid. It is determined by heating the fat with neutral alcohol which dissolves the fatty acids, and titrating to neutrality by standard acid.

C. On heating an animal or vegetable fat with a solution of a caustic alkali it is saponified, *i. e.*, the constituent glycerides are successively converted into fatty acid salts of the alkali with the production of glycerol, the radical C_3H_5 exchanging with the alkali metal; thus in the case of stearin —

$$(C_3H_5)(C_{18}H_{35}O_2)_3 \text{ (stearin)} + 3KOH = K_3(C_{18}H_{35}O_2)_3 \text{ (potassium stearate)} + (C_3H_5)(OH)_3 \text{ (glycerol)}.$$

So that for 890.88 grams of pure stearin there is required 168.354 grams of potassium hydrate; or one liter of normal solution of potassium hydrate (56.118 grams KOH per liter) will saponify $890.88 \times 56.118 \div 168.354 = 296.96$ grams of stearin, and by a similar calculation, 294.94 grams of olein, and 268.93 of palmitin.

The number of grams of a fat or oil saponified by one liter of normal potassium hydrate is called its *saponification equivalent;* for pure anhydrous lard it lies between 286 and 292, for cotton-seed stearin from 285 to 294, cocoanut oil, 209 to 228, butter-fat, 241 to 253, etc. The *Koettstorffer Number* is the number of milligrams of KOH required to saponify one gram of anhydrous fat — it is simply another way of expressing the saponification equivalent. In both cases there is required an equivalent of alkali for both the decomposition of the fats and the neutralization of the associated free fatty acids.

The saponification is effected by boiling the fat with an excess of a standard solution of caustic potash in alcohol (the alcohol takes no direct part in the reaction but attacks the fat much more energetically than an aqueous solution) and determining the uncombined alkali by titration with a standard acid and phenol-phthalein, this indicator being unaffected in a cold solution by the potassium fatty acid salts. The weight of alkali taking part in the reaction is found by difference.

D. After titration, the fatty acids combined with potassium are set free by the addition of a mineral acid, *e. g.*, hydrochloric —

$$\underset{\text{Potassium oleate.}}{KC_{18}H_{33}O_2} + HCl = \underset{\text{Oleic acid.}}{C_{18}H_{33}O.OH} + KCl.$$

The mixed fatty acids (insoluble in water and mineral acids) are filtered, washed with water, dried and weighed, one gram of dry lard giving about .962 grams, and of cottonseed stearin, .955 grams.

A. Water. A large beaker is weighed and about 50 grams of fresh lard introduced. The beaker is heated to 105° for an hour, cooled and reweighed; the loss is water.

B. Free acid. Fifty grams of the undried lard is weighed into a beaker, covered with 50 Cc. of *neutral* (page 207) alcohol, and heated to boiling. The mixture is then titrated with standard potassium hydrate and phenol-phthalein, taking care that the red color persists after vigorous stirring. The presence of the undissolved lard does not interfere. The reaction is assumed to be

$$H_3(C_{18}H_{33}O_2)_3\ (846.816) + 3KOH(168.354) = K_3(C_{18}H_{33}O_2)_3 + 3H_2O.$$

Oleic acid. Potassium oleate.

C. Saponification equivalent. An alcoholic solution of potassium hydrate containing about 15 grams of KOH in 300 Cc. is prepared as follows: About 3 grams of stick potash is weighed and dissolved in water and titrated with standard sulfuric acid, and the following proportion solved,

Cubic centimeters of acid required, times the weight of KOH neutralized by one Cc. : weight of potash taken : : 15 grams : x.

Then x grams of the potash is dissolved in 300 Cc. of strong alcohol and the solution filtered into a glass-stoppered bottle.

Three No. 3 beakers * are weighed and about 8 grams of the dried lard from A introduced in each and accurately weighed. Into each beaker and two others of the same size, is run 50 Cc. of the potash solution, allowing five drops to drain from the pipette to secure a uniform measure. The five beakers are then covered with watch-glasses and boiled gently for fifteen minutes. After cooling, the beakers are three-fourths filled with cold water, stirred until clear, and *cautiously* titrated with standard sulfuric acid and phenol-phthalein until the red color has just changed to yellow.

D. Fatty acids by weight. Each of the three solutions is treated as follows: To expel the alcohol the solution is evaporated nearly to dryness on the water bath, and after diluting with hot water to dissolve the soap dried on the surface, hydrochloric acid is poured in until the reaction is decidedly acid and the fatty acids clot and form one mass on stirring. The beaker is then heated on the water bath until the fatty acids melt, and digested in a warm place, preferably over night, until the solution of glycerol and potassium salts is clear.

A close filter of 12.5 Cm. diameter is inclosed in a small beaker, covered with a watch-glass, dried at 100° and weighed; the filter is fitted to a funnel, half filled with hot water, and the solution filtered. The paper must never be much more than half filled at any time, and the operation should continue uninterruptedly. The beaker is rinsed and the filter washed with boiling water a few times, and the funnel lowered into cold water to congeal the fatty acids.

The ring of fat adhering to the beaker and rod is dissolved in a little hot alcohol which is poured into the small beaker and evaporated to dryness. The filter is removed from the funnel and opened on blotting paper to partially dry it. The cone of fatty acids is then dropped in the small beaker, followed by the filter. After drying at 100° for an hour, the beaker is covered with the watch-glass, cooled and weighed. The drying and weighing are repeated, and if the loss does not exceed a few milligrams, the fatty acids may be considered free from water.

Calculation. The difference between the volume of acid used for the lard, and that for the average of the blanks, times the KOH equivalent of 1000

* Chem. News, 1891—1—82.

Cc. of the standard acid, divided by the weight of dry lard taken, gives the Koettstorffer Number; and 56118 divided by this number gives the saponification equivalent. One gram of KOH neutralizes 5.033 grams of oleic acid.

Example.

A.	Weight of lard			49.168 grams.
	Loss on drying			.052 "
	Percentage of water			.11
B.	Weight of lard			50.000 grams.
	Volume of standard KOH for neutralization			.5 Cc.
	One Cc. contains of KOH			.05882 gram.
	Free fatty acids expressed as oleic			.30 per cent.
		A.	*B.*	*C.*
C.	Weight of dry lard	8.314	9.620	9.010
	Volume of standard acid	19.1 Cc.	14.8 Cc.	16.7 Cc.
	For 50 Cc. alcoholic potash	46.2 Cc.	46.2 Cc.	.....
	KOH equivalent of acid	.0593		
	Koettstorffer Number	193.3	193.5	194.1
	Saponification equivalent	290.3	290.0	289.1
D.	Weight of fatty acids	7.969	9.233	8.632
	Percentage of fatty acids	95.85	95.98	95.80

EXERCISE 21 — POTASSIUM PERMANGANATE.

Complete Analysis.

On heating potassium permanganate with hydrochloric acid, the potassium and manganese become chlorides, the other products of the reaction being chlorine and water —

$$K_2Mn_2O_8 + 16HCl = 2KCl + 2MnCl_2 + 5Cl_2 + 8H_2O.$$

The potassium is determined by precipitation as potassium platinchloride, and the manganese by precipitation as manganous ammonium phosphate; the oxygen by its reaction with a ferrous salt.

1. Potassium chloride forms with chloroplatinic acid a yellow or red crystalline compound — $2KCl + H_2PtCl_6 = K_2PtCl_6 + 2HCl$. This precipitate is soluble in 100 parts of cold water, about 4000 parts of alcohol of 80 per cent, and 12000 parts of absolute alcohol. Manganous chloride does not combine with this reagent, and is easily soluble in both water and alcohol; the two metals may therefore be separated in this way, using alcohol to decrease the solvency of the precipitate.

On igniting the precipitate there remains $2KCl + Pt$, chlorine escaping. The precipitate may be dried at 105° without change.

2. After precipitating the potassium the manganese could be determined in the filtrate, but as the excess of platinic chloride is troublesome to remove, it is preferable to operate on another portion of the permanganate.

Manganous chloride is precipitated by ammonium phosphate as manganous ammonium phosphate —

$$MnCl_2 + NaNH_4HPO_4 + NH_4OH = MnNH_4PO_4 + NaCl + NH_4Cl + H_2O.$$

First appearing in white flocks, but condensing on boiling or long standing in presence of a large excess of the precipitant, to rose-colored scales. The precipitate is soluble in acids but insoluble in water and dilute ammonia. On ignition there is left manganese pyrophosphate, in the form of a white crust fusible at a bright red heat — $2MnNH_4PO_4 + \text{heat} = Mn_2P_2O_7 + 2NH_3 + H_2O$.

3. The five atoms of oxygen are determined volumetrically by their power of decomposing sulfuric acid in presence of a ferrous compound —

$$K_2Mn_2O_8 + 8H_2SO_4 + 10FeSO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

An excess of a standard solution of ferrous sulfate is oxidized by a given weight of the sample, and the remaining ferrosum found by titration by standard permanganate.

Select a few grams of small, clean, well-formed crystals, break to a coarse powder in a mortar, and preserve in a stoppered tube.

1. Determination of potassium. Weigh exactly about .5 gram and transfer to a two-ounce beaker. Dissolve in 20 Cc. of hot water, cover the beaker and slowly add 5 Cc. of concentrated hydrochloric acid. Boil gently until the solution is nearly colorless, shaking the beaker to wash down any manganic hydrate that may collect on the sides.

Precipitate the potassium by a volume of solution of chloroplatinic acid containing about one gram of platinum. Evaporate on the water bath just to dryness.

Moisten the residue with a few drops of water, add 20 Cc. of alcohol of about 85 per cent, and stir well. Decant on a 7-Cm. filter keeping the precipitate in the beaker. Wash a few times by decantation with alcohol containing a few drops of the reagent, then transfer to the filter and wash with alcohol alone. After drying on the water-bath, shake and brush the precipitate into a tared watch-glass or weighing-bottle, dry for a half hour at 105°, and weigh. The filter retaining a little precipitate is burned in a platinum crucible and the ash weighed.

A Gooch crucible may be used with advantage for this determination.

The results are apt to be a trifle low from the solubility of the precipitate in alcohol. Care should be taken to prevent access of ammonia fumes to the solution as ammonium platinchloride may be formed.

2. Determination of manganese. Weigh about one gram of the sample, transfer to an eight-ounce beaker and dissolve in 50 Cc. of hot water. While gently boiling add cautiously about 15 Cc. of concentrated hydrochloric acid and boil until the liquid is a clear yellow.

Dissolve in a porcelain dish about ten grams of sodium ammonium phosphate in 100 Cc. of warm water plus a few drops of ammonia. Filter the solution into the manganese solution, and heat the latter to boiling. Now add a few cubic centimeters of sulfurous acid, then ammonia to decided alkaline reaction. Stir for a few minutes and set aside in a warm place until the precipitate becomes entirely crystalline, which may require an hour or more. Filter through a 12.5 Cm. paper, wash thoroughly with cold water containing a few drops of ammonia, burn the filter containing the precipitate in a platinum crucible, ignite to dull redness, and weigh as manganese pyrophosphate.

3. Determination of oxygen. Weigh between .200 and .250 gram of the sample and transfer to an eight-ounce beaker. Add about 100 Cc. of cold water, exactly 100 Cc. of the standard ferrous solution (page 229), and 25 Cc. of dilute sulfuric acid; stir until dissolved, and immediately titrate the excess by standard permanganate.

Calculation.

1. Potassium oxide —

$$\begin{cases} \text{In the precipitate,} & K_2PtCl_6 : K_2O :: 485.82 : 94.22. \\ \text{With the filter,} & 2KCl + Pt. : K_2O :: 344.02 : 94.22. \end{cases}$$

2. Manganese oxide. $Mn_2P_2O_7 : 2MnO :: 284 : 142.$

3. Available oxygen. This may be computed in several ways. In the following we find not the percentage of oxygen in the sample itself, but that in

such a volume of the standard solution of permanganate as exactly equals it in action on ferrous sulfate.

Let a be the weight of the sample, and b the weight of iron oxidized by one cubic centimeter of the standard permanganate. From the equation *ante* we see that 10 atoms of iron (560) react with 5 atoms of oxygen (80), or in the ratio of 7 of iron to 1 of oxygen, hence $\frac{b}{7}$ is the weight of oxygen in one cubic centimeter of the standard permanganate.

Let c be the volume of standard permanganate used in titrating 100 Cc. of the ferrous solution; and d, the volume used for the excess in the determination. Then $c - d$ is the volume of standard permanganate of equal oxidizing power to a, and $(c - d) \times \frac{b}{7}$ is the weight of oxygen in $c - b$.

Therefore $(c - d) \times \frac{b}{7} \times \frac{100}{a}$ is the percentage of available oxygen in a.*

Example. In an exceptionally pure commercial article was found —

1. Weight of sample .5014 gram. The potassium platinchloride weighed .7715 gram, and the residue in the filter .001 gram. Therefore the percentage of potassium oxide was 29.89.

2. Weight of sample 1.0155 grams. The manganese pyrophosphate weighed .9137 gram. Therefore the manganous oxide was 44.98 per cent.

3. Weight of sample .2624 gram. One hundred Cc. of the ferrous solution contained .5098 gram of iron, and required 72.3 Cc. of the standard permanganate. In the determination the excess of ferrous solution required 6.8 Cc. of permanganate. Therefore the available oxygen was 25.14 per cent.

	Found.	In theory.
Potassium oxide.....	29.89	29.80
Manganese oxide.....	44.98	44.90
Available oxygen.....	25.14	25.30
	100.01	100.00

EXERCISE 22—A. DETERMINATION OF NITROGEN IN AIR.

The atmosphere contains by volume from 20.96 to 20.99 per cent of oxygen, the remainder being nitrogen with a little water vapor and carbon dioxide and traces of ammonia, nitrous acid, etc. The normal proportion of carbon dioxide is from .03 to .06 per cent but in a confined space may be considerably augmented by combustion, respiration or fermentation.

Oxygen and carbon dioxide are simultaneously absorbed by a solution of pyrogallin in potassium hydrate, leaving nitrogen as a residue. A measured volume of air is brought in contact with this reagent and the residual nitrogen measured; the operation may be performed in any form of gas-absorption apparatus, of which the one devised by Bunte is here employed. It is made entirely of glass and consists of a tube A, Fig. 139, of such a size that it contains 100 Cc. from the plug of the stopcock B to the zero C, and is divided into cubic centimeters and tenths. The stopcock B is of the form known as a "three-way," since according to the position of the plug it opens a passage from A to D or from A to E, or closes all three. An ordinary stop-cock F

* Crookes Select Methods, 1 *et seq.*; Amer. Journ. Science, 1899—206; School of Mines Quart. 11—355; Journ. Amer. Chem. Socy. 1895—453.

terminates the burette below. An aspirator bottle G, filled with water, is connected with F by a long rubber tube H. The burette is held vertically in two clamps fixed on the rod of a retort stand.

Filling the burette. The stopcocks are opened and G raised until the burette is filled with water; G is lowered until the surface of water it contains is at a level with the zero mark C. The stop-cock B is turned so as to close all the exits; then F is closed and the tube H removed. The burette now contains 100 Cc. of moist air at the temperature of the laboratory and the pressure of the surrounding atmosphere.

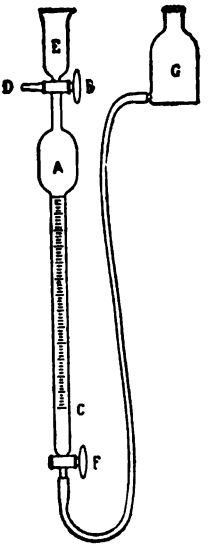

Fig. 189.

Into the funnel E is poured 25 Cc. of the pyrogallate solution (page 210); the stopcock B is turned so that a little of the solution enters the burette; as the oxygen is absorbed more of the solution enters to replace it. After closing B the burette is removed from the stand, held horizontally, and rotated to bring any unabsorbed oxygen in contact with the reagent.

The burette is returned to the support and E filled with water; the cock B is opened slightly, and when no more water enters the burette, F is also partly opened. The slow stream of water flowing through the burette washes out the reagent, E being replenished with water until that leaving F is nearly colorless. B is then closed and the tube H slipped over the tube of F taking care that H is entirely filled with water before so doing. F is opened and G raised until the surfaces of water in it and the burette are at a level. After standing for 15 minutes, the volume of residual nitrogen is read.

Care must be taken that no air enters or gas escapes from the burette during these operations, and that the temperature of the laboratory does not materially change during the analysis.

Calculation. Let N be the percentage of nitrogen in the air; V, the original volume of air; v, the volume of moist nitrogen remaining after absorption of the oxygen and carbon dioxide; then $N = \frac{100}{V}$. No account is taken of the temperature, pressure, or tension of aqueous vapor, since these are identical or nearly so in both readings.

Example. Three experiments on 100 Cc. of pure air gave 79.3, 79.3 and 79.4 per cent of nitrogen.

A substitute for the Bunte burette may be contrived by closing the top of an ordinary burette by a cork holding a funnel-tube with a glass stopcock. The volume of the space between the plug of the stopcock and the zero of the burette is ascertained by filling the burette with water and drawing what is contained between these two points into a small measuring-jar; this volume is to be included in the calculation of the result of a determination.

B. AMMONIUM SULFATE.

Determination of Nitrogen.

Ammonium sulfate crystallizes in anhydrous colorless needles soluble in 1.8 parts of cold and an equal weight of hot water. The commercial salt may be purified by stirring 100 grams in 100 Cc. of boiling water, filtering hot, and

allowing to cool slowly. The crystals deposited are drained and pressed in filter paper until apparently dry, and preserved in a desiccator over sulfuric acid. The pure salt contains 21.24 per cent of nitrogen.

The determination is made by setting free the nitrogen measuring its volume and calculating its weight.

1. When bromine is mixed with a strong solution of sodium hydrate there are formed sodium bromide and sodium hypobromite —

$$2NaOH + Br_2 = NaBr + NaOBr + H_2O.$$

2. Ammonium sulfate is decomposed when brought in contact with sodium hydrate, forming free ammonia, sodium sulfate, and water —

$$(NH_4)_2SO_4 + 2NaOH = Na_2SO_4 + 2NH_3 + 2H_2O.$$

3. Sodium hypobromite reacts with ammonia to form nitrogen, which being nearly insoluble in water, is evolved —

$$2NH_3 + 3NaOBr = N_2 + 3NaBr + 3H_2O.$$

4. The volume of nitrogen is found by the increase in volume of a fixed, though unmeasured, volume of air when the two are united; the increase, measured in cubic centimeters when saturated with aqueous vapor and at the temperature and pressure of the atmosphere at the time of the experiment, is reduced to standard conditions (page 183) and multiplied by the weight of one cubic centimeter of nitrogen under these conditions (.0012562 gram).

5. Since the nitrogen is evolved into a certain volume of air, the amount retained by the solution generating it is proportional to the volume of nitrogen given off. Under the conditions detailed below the volume retained amounts to about .5 Cc.

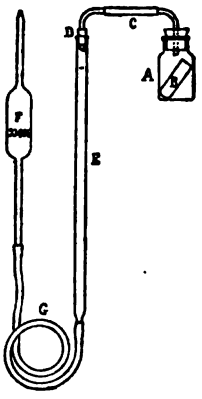

Fig. 140.

The apparatus for the test is fitted up as shown in Fig. 140. A is a wide-mouth bottle of about 175 Cc. capacity; B, a test tube of ½ inch diameter cut off to such a length as will stand in the bottle in an inclined position as shown. A rubber stopper closes A and holds a bent glass tube connected by a short rubber tube C to the tube D which fits in a stopper inserted into the top of a 50 Cc. burette E. The bottom of the burette is joined to a 100 Cc. pipette F by a long rubber tube G.

The burette and pipette are held firmly in clamps of a burette stand, and A is provided with a rest at the proper height.

A solution of sodium hydrate is prepared by dissolving 40 grams of commercial caustic soda in 100 Cc. of water; after cooling 10 Cc. of bromine is added and stirred until dissolved. This solution is kept in a stoppered flask: it retains its activity for a few days only.

The room in which the analysis is made should not be liable to sudden changes of temperature. F is supported close to the burette, at such a height that the zero mark is opposite the middle of the bulb and water is poured into E until it rises to the zero mark. Twenty-five Cc. of the hypobromite solution is poured into A.

The test-tube B is dried and supported in the stand Fig. 30, and the two weighed together; about .200 gram of the ammonium sulfate is placed in the tube and the stand and tube again weighed. About ten Cc. of water is carefully poured into the tube and shaken around until the salt is dissolved, then the tube lowered into the bottle A. The stoppers are firmly inserted in the bottle and burette and the apparatus left undisturbed for a half-hour that the liquids may come to the room temperature.

On returning, the operator adjusts the water levels, reads the burette, and records the temperature and barometric pressure of the air of the room. Holding the bottle in the left hand and F in the right, he inclines A until some of the solution in the tube flows into the bottle; at the same time he lowers F so as to keep the levels of water in the burette and pipette about the same, this tending to prevent leakage of air or gas from connections not perfectly tight. When all the solution has run from B, A is quickly turned upright in order that B may partly fill with the hypobromite solution.

F is now supported at such a height that the levels of water are the same and the apparatus left to cool for an hour. The levels of water are then accurately adjusted and the volume read, and the barometer and thermometer again noted to discover any variation from the former reading.

Calculation. The following formula embodies the principles stated on page 183.

$$N = (V + .5\ \text{Cc.}) \times (B - F) \times \frac{.0012652}{760\ (1 + .00367t)} \times \frac{100}{S}$$

in which N is the percentage of nitrogen in the salt; V, the observed volume of gas; .5 Cc., the correction for absorption of nitrogen in the liquid; B, the height of the barometer in millimeters; F, the tension of aqueous vapor at the observed temperature; t, the temperature of the room in degrees Centigrade; and S, the weight of the sample. The computation may be facilitated by the tables at the end of the volume.

Example.

	A.	B.	C.
Weight of ammonium sulfate	.2016	.2047	.1996
Reading of burette before evolution	.6 Cc.	.6 Cc.	.4 Cc.
Reading of burette after evolution	37.7 Cc.	39.0 Cc.	37.9 Cc.
Volume of nitrogen (uncorrected)	37.1 Cc.	38.4 Cc.	37.5 Cc.
Height of barometer in millimeters	762	760	762
Temperature of room in degrees Cent.	23.0	24.5	26.0
Percentage of nitrogen	21.07	21.25	21.17

Results are usually somewhat below the theoretical (21.24) by reason of the formation of small amounts of nitrogen compounds not decomposed by the hypobromite solution.

EXERCISE 28 — NICKEL — COPPER ALLOY.

A. Determination of the Metals Gravimetrically.

Both nickel and copper, as well as the small amount of iron generally present, are readily soluble in nitric acid, leaving the sulfates on evaporation with sulfuric acid. In the following method the copper is precipitated as cuprous sulfocyanide, roasted to cupric oxide; and the nickel in the filtrate as nickelic hydrate, ignited to nickelous oxide.

1. Cupric sulfocyanide, $Cu_2(CNS)_4$, is a black precipitate thrown down by potassium sulfocyanide; in presence of a reducing agent it is transformed to cuprous sulfocyanide —

$$2CuSO_4 + 2KCNS + H_2SO_3 + H_2O = 2CuCNS + K_2SO_4 + 2H_2SO_4.$$

The cuprous sulfocyanide is a white or pale rose-colored powder, insoluble in very dilute acids, but slightly decomposed by water. On ignition with free access of oxygen, there remains cupric oxide with a little cuprous sulfide; this is converted into sulfate by solution in nitric and sulfuric acids, which leaves pure cupric oxide on evaporation and strong heating.

* Allen, Coml. Org. Anal. 3—3—263.

2. Nickel is not precipitated by a sulfocyanide, but gives green nickelous hydrate with the fixed alkalies; if chlorine or bromine be present, the precipitate comes down mainly as black nickelic hydrate, insoluble in alkalies and water —

$$2NiSO_4 + 6KOH + Cl_2 = Ni_2(OH)_6 + 2K_2SO_4 + 2KCl.$$

On ignition there pass off water and oxygen, leaving nickelous oxide (NiO). This contains the iron of the alloy and is also liable to be contaminated with silica coming from the alkali or dissolved from the vessels used.

3. Copper and nickel form soluble double salts with excess of ammonia, while ferric iron is precipitated as a hydrate, $Fe_2(OH)_6$. On ignition this is converted into ferric oxide, Fe_2O_3.

Clean one five-cent coin of recent issue, and after weighing dissolve in a large, tall beaker or flask in a mixture of 100 Cc. of water and 50 Cc. of concentrated nitric acid. Cool the solution and add 100 Cc. of dilute (ten per cent) sulfuric acid, and 500 Cc. of cold water. Pour into a one-liter measuring flask and make up to the mark with water, rinsing the beaker with water.

Copper.

Pipette 50 Cc. of the solution into a 12-oz. beaker, heat to near boiling and add dilute solution of sodium carbonate until a *slight* permanent precipitate of copper hydrate is formed; dissolve this in 75 Cc. of strong sulfurous acid water, and precipitate by adding a slight excess of potassium sulfocyanide. Let stand in a warm place for half an hour, occasionally stirring, and pass through a double filter, receiving the filtrate in a large beaker. Wash with a mixture of one volume of sulfurous acid water with nine volumes of water. Inclose the precipitate in the paper and heat gently in a weighed platinum crucible. After the paper has charred, incline the crucible, and roast at a dull red heat until no more sulfurous acid escapes.

Cool the crucible, add one or two Cc. of water, five or six drops of concentrated sulfuric acid and a few drops of nitric acid. Heat until solution takes place, evaporate to dryness on the water bath and drive off the excess of acid by heat gradually increased to redness. Weigh quickly, as the copper oxide is somewhat hygroscopic.

Nickel.

Transfer the filtrate and washings to a casserole or porcelain dish, add five Cc. of concentrated nitric acid, cover, and boil under the hood until effervescence ceases. This decomposes the excess of potassium sulfocyanide which would interfere with the precipitation of the nickel.

After the addition of 50 Cc. of bromine water, make slightly alkaline with pure potash solution, freshly made. Boil for a few minutes, allow to settle, filter, and wash thoroughly with hot water. Burn the filter with the precipitate in a platinum crucible, heat to bright redness and weigh as NiO. If a hydrogen generator is at hand, ignite in a current of the gas, reducing the oxide to the metal.

The oxide is brushed into a small beaker, dissolved by heating with concentrated hydrochloric acid, and evaporated to dryness with a little sulfuric acid. The residue is dissolved in hot water and filtered from any silica that may remain. The silica is ignited and weighed and the weight subtracted from that of the nickel oxide, as is also that of one-fourth of the ferric oxide found below.

Iron.

Draw 200 Cc. from the flask to a porcelain dish, heat to boiling and precipitate by a slight excess of ammonia. After filtering through a small paper and washing with hot water, the ferric hydrate is dissolved into a small beaker by washing the filter with hot dilute hydrochloric acid, and again precipitated by ammonia to free it entirely from the other metals. After filtration and thorough washing, it is ignited with the filter in a platinum crucible, and weighed as Fe_2O_3.

Calculation.

Fe_2O_3	: Fe_2	: :	160.00	: 112.00.
CuO	: Cu	: :	79.60	: 63.60.
NiO	: Ni	: :	74.70	: 58.70.

Example.

Weight of			Per cent.	
Coin	4.886	grams;		
Ferric oxide	.0008	"	Iron	.06
Cupric oxide	.2300	"	Copper	75.22
Nickel oxide	.0785	"	Nickel	24.77
(less SiO_2 .0013, and Fe_2O_3, .0002)				

B. Electrolytic determination.

On connecting plates of platinum with the poles of a galvanic battery, and immersing them in an acid solution of copper sulfate, the copper will be slowly deposited on one of them as a closely-adhering film, while oxygen separates at the other. Nickel is not deposited from an acid solution, but when this is made ammoniacal it separates in the same manner as copper.

The battery may be any form giving a continuous constant current proportioned to the amount of metal to be deposited, resistance of the solution, etc. There may be used either three 'gravity,' or two Edison-Lalande cells (or a current from an incandescent light wire reduced by a resistance coil or incandescent bulbs, or a storage battery). A very effective form is a one-gallon Bunsen cell consisting of a carbon rod standing in a porous clay cup surrounded by a cylinder of zinc, the whole set in a glass jar about six inches diameter by eight inches high. One of these will precipitate the copper from one or two solutions, and runs for 24 hours with one charge of battery fluid—essentially a solution of chromic acid, page 207.

The electrodes may be in the form of small cylinders, Fig. 141, with heavy wires fused to them to connect to the battery wires. The deposition is made in a tall 12-oz beaker. To prevent a partial re-solution of the deposited metal, the current must continue until the cathode has been removed from the solution.

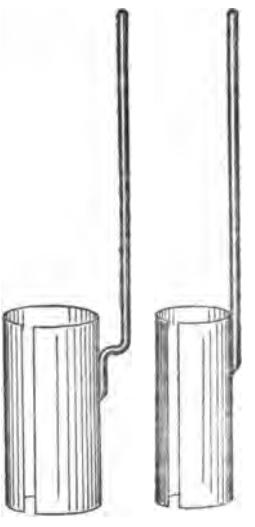

Fig. 141

Heat the larger cylinder to redness and weigh when cool. Hang them concentrically, about one-eighth inch from the bottom of the beaker, connecting their wires by binding-screws to the wires from the battery as shown in Fig. 142, taking care

that the ends entering the binding-screws and the interior of the latter are clean and bright.

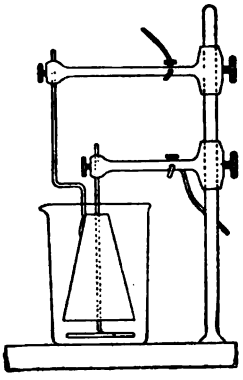

Fig. 142.

In the evening withdraw 100 Cc. of the solution of the coin and run it into the beaker. Add water until the cylinders are covered and mix well. Charge the battery by nearly filling the porous cup with the battery fluid, and the glass jar to the same height with water. Observe that the platinum cylinders are not in contact and that the connections are screwed tightly together. Cover the beaker with two plates of glass, and the whole apparatus with a sheet of paper to exclude dust.

On the following morning the copper will be found deposited, probably completely, on the outer cylinder; it should have a clean bright red color. Add a little water and mix with a glass rod, so as to expose an uncoated surface of platinum, and if no copper is deposited thereon in a half hour, the separation is complete.

Two beakers, large enough to contain the cathode, are filled with distilled water; the cathode is transferred as rapidly as possible from the solution to one of the beakers, then to the other; drained, dried in the oven for a few minutes at 100°, cooled and weighed. Or it may be finally rinsed with strong alcohol, drained and touched with a flame; when the alcohol has burned the cylinder is weighed.

Nickel.

Unite the waters used for washing the cylinders with the solution of the nickel sulfate, evaporate the whole to dryness to expel nitric acid, and heat till sulfuric fumes arise. Cool, dissolve in 100 Cc. of hot water, and transfer to the beaker used in precipitating the copper.

The battery is emptied, and the copper dissolved from the cathode by nitric acid. The cathode is weighed, the two cylinders connected up as before, and the battery recharged. Add to the nickel solution 30 Cc. of concentrated ammonia, and hot water until the cylinders are covered. The remainder of the operation is conducted substantially as directed for the copper.

Iron.

The iron is determined colorimetrically. It is separated from the nickel and copper by precipitation of the former by ammonia, filtered, and the precipitate dissolved in a little dilute nitric acid. The iron is converted into sulfocyanide by an excess of potassium sulfocyanide, and the depth of the red color of the ferric sulfocyanide is matched by one containing a known weight of iron in an approximately equal volume of solution.

Prepare a solution of ferric nitrate of known concentration by dissolving .010 gram of iron wire in a little dilute nitric acid, and boiling for a few minutes; cool and transfer to a measuring-jar and dilute to 100 Cc. Rinse and fill a burette with the solution.

Measure 100 Cc. of the solution of the coin into a small beaker and precipitate the iron exactly as directed on page 249. Dissolve the second ferric hydrate precipitate on the filter by running through a little dilute nitric acid, letting the solution run into a comparison tube; wash the filter with water, and dilute the filtrate and washings to 30 to 40 Cc. Into the other comparison tube put about as much water and add to each two Cc. of solution of potassium

sulfocyanide. Immediately run into the second tube sufficient iron solution to cause the tints to appear equal, or each tube darker when held to the left of the other. The comparison may be made by holding the tubes close together, at an angle of 45° over a sheet of white paper facing a window, viewing them against a clear sky, or otherwise as is found most suitable for the vision of the comparer. Read the volume of iron solution used and the volume in each of the comparison tubes.

Calculation. Let A be the volume of solution in the first tube; B, the volume in the second tube; C, the volume of iron solution added to B; W, the weight of the coin; b, the weight of iron in A; and X, the percentage of iron in the alloy. Then .0001 C is the weight of iron in B, and $A : B :: b : .0001\ C$.

Hence $b = \frac{.0001\ CA}{B}$ and $X = \frac{.0001\ C.A \times 1000 \times 100}{100\ B.\ W}$

Example.

Weight of coin	4.990 grams.
Volume of solution in first comparison tube	41.0 Cc.
Volume in second tube	47.0 Cc.
Volume of iron solution added to second tube	4.4 Cc.
Percentage of iron in the coin	.08
Weight of cylinder and copper	22.0885 grams.
Weight of cylinder	21.7135 "
Weight of copper	.3750 "
Weight of cylinder and nickel	21.8378 "
Weight of cylinder	21.7133 "
Weight of nickel	.1245 "

	Gravimetrically.	Electrolytically
Copper	75.22	75.15
Nickel	24.77	24.95
Iron	.06	.08
	100.05	100.18

References. Journ. Anal. Chem. 1889—342. Journ. Anal. Appl. Chem. 5—133 and 184. Zeits. Anal. 19—314. Chem. News, 1894—1—17. *Idem*, 1893—2—215.

EXERCISE 24 — SILICATES.

A. Decomposed by Hydrochloric Acid — Wollastonite.

Wollastonite is a silicate of calcium, $CaO.SiO_2$, crystallizing in the oblique system; color white or light shades. Usually it contains as impurities small amounts of the oxides of iron, aluminum, manganese and magnesium, sometimes alkalies and combined water.

In the following scheme the hydrochloric solution of the mineral is first freed from silica by evaporation, then each base successively thrown down by an appropriate precipitant. Alkalies and water are determined in separate portions of the mineral.

1. The powder is decomposed by dilute hydrochloric acid, the silica mainly passing into solution, and the bases forming soluble chlorides. On evaporation of this solution to dryness the chlorides remain unchanged, while the silica becomes practically insoluble in acids and water. On filtering and drying the silica it appears as a light, loose, white powder, infusible and unaffected by ignition. As a small portion of the mineral may have resisted the acid, after

weighing the silica it is evaporated with hydrofluoric and sulfuric acids, the silica passing off as the gaseous compound hydrofluosilicic acid, while the residue is a mixture of sulfates of the bases. This residue is weighed, dissolved in hydrochloric acid, and added to the filtrate from the silica; the weight is also subtracted from that of the impure silica — a slight error is here introduced from the presence of the sulfuric radical.

2. The addition of an excess of ammonia to a solution of ferric chloride precipitates the metal as ferric hydrate insoluble in water and ammonia, but easily soluble in acids — $Fe_2Cl_6 + 6NH_4OH = Fe_2(OH)_6 + 6NH_4Cl$. The hydrate loses water when ignited and becomes ferric oxide; if ammonium chloride be not completely washed out there is a slight loss from formation of volatile ferric chloride.

Aluminum chloride shows a similar behavior to ferric. In either case any traces of silica in the solution are carried down mechanically with the precipitate.

3. Ferric and aluminum oxides are slowly but completely soluble in concentrated sulfuric acid when hot, silica remaining. After filtering, the ferric sulfate is reduced by zinc and titrated by weak standard permanganate. The iron found is calculated to ferric oxide, the weight of the residual silica added, and the sum subtracted from the original weight; the remainder is the alumina.

4. Manganous, calcium, and magnesium chlorides are transformed to acetates on the addition of an alkali acetate. Manganous acetate is decomposed when heated with bromine and ammonia, insoluble (hydrated) manganic oxide being precipitated — *e. g.*

$$2Mn(C_2H_3O_2)_2 + 5Br_2 + 16NH_3 + 4H_2O = 2MnO_2 + 10NH_4Br + 4NH_4C_2H_3O_2 + N_2.$$

On ignition the precipitate loses water and oxygen and becomes trimanganic tetroxide — $3MnO_2.H_2O = Mn_3O_4 + O_2 + H_2O$.

5. Neither calcium nor magnesium acetate is precipitated by these reagents. Calcium is precipitated as calcium oxalate by ammonium oxalate; magnesium oxalate remains in solution nearly completely; if in large quantity usually a small part comes down with the calcium oxalate, but can be removed by redissolving the filtered precipitate and reprecipitating with ammonia.

On igniting calcium oxalate below redness there escapes carbon monoxide leaving calcium carbonate; at bright redness carbon dioxide is driven off from the carbonate leaving calcium oxide as a white powder, quite hygroscopic.

6. In the filtrate from the calcium oxalate the magnesium is precipitated by ammonium phosphate as magnesium ammonium phosphate, it slowly depositing in a crystalline or semi-crystalline powder which tends to adhere closely to the sides of the vessel especially where rubbed with a glass rod. The precipitate is soluble in mineral acids, insoluble in dilute ammonia, and on ignition is converted into magnesium pyrophosphate with evolution of water and ammonia —

$$2MgNH_4PO_4 + \text{heat} = Mg_2P_2O_7 + 2NH_3 + H_2O.$$

The pyrophosphate is left as a crisp white mass, soluble in mineral acids with reconversion to the orthophosphate.

7. A silicate decomposes when ignited with calcium chloride and oxide to form silicates of calcium and other bases insoluble in water, and chlorides of the alkalies. On lixiviation with water, the chlorides are extracted, together with calcium chloride and a little calcium hydrate. In the filtrate, the calcium is precipitated by ammonium carbonate, leaving only alkali salts in solution; on evaporation and ignition the ammonium salts escape. The chlorides of potassium and sodium are weighed as such, and may be separated by precipitation of the former by platinic chloride (page 243); or the chlorine may be

determined in the mixture, and the proportions of the metals calculated therefrom (page 179).

8. Water of combination is found from the loss in weight on ignition to redness. This will also include any organic matter or carbon dioxide contained in the mineral.

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1. Silica. Select pure fibers of the mineral and grind a few grams to a very fine powder in an agate mortar. Dry at 100° and weigh one gram and transfer to a porcelain or platinum dish or a casserole. Cover with 100 Cc. of boiling water and decompose by 25 Cc. of concentrated hydrochloric acid added slowly with constant stirring. When no more grit can be felt with a glass rod, evaporate on the water-bath to dryness; moisten with concentrated hydrochloric acid and again evaporate to complete dryness.

The residue is moistened with a little concentrated hydrochloric acid and a few drops of nitric acid, diluted with 100 Cc. of hot water, and filtered into a porcelain dish, washing the silica on the filter with hot water until the washings show no cloud with silver nitrate. The filter is opened on a porous tile and then wrapped around the precipitate, burned in a platinum crucible and ignited to a white heat.

The purity of the silica is tested by moistening it with water in the crucible, then adding about 5 Cc. of pure hydrofluoric acid and a drop of sulfuric acid; the liquid is evaporated to dryness and the crucible heated to redness. If there remains only a few milligrams of residue it is again evaporated with a little hydrofluoric acid, weighed and dissolved in hydrochloric acid and the solution added to the original filtrate. But if the residue is considerable it is evident that the mineral was not ground finely enough, and the analysis is recommenced with a finer powder.

2. Iron and aluminum oxides. Heat the filtrate to boiling and precipitate by ammonia, using but a slight excess. Boil until the smell of ammonia is gone, allow to settle, and pass through a small filter; to prevent access of carbon dioxide from the air — which would precipitate calcium — keep the funnel and dish closely covered. Wash a few times with hot water, then dissolve the precipitate by washing the filter alternately with hot dilute hydrochloric acid and hot water, letting the solution run into the porcelain dish. The solution is now precipitated by ammonia as before, filtered and washed thoroughly. The precipitate is wrapped up in the paper and the latter burned, finally igniting the precipitate, not higher than dull redness. It is weighed as $Fe_2O_3 + Al_2O_3 + SiO_2$.

3. Iron oxide. The precipitate is brushed into a small beaker and 20 Cc. of dilute (10 per cent) sulfuric acid added; then evaporated until fumes of sulfuric acid arise. After dilution with water and repeating the evaporation and dilution, usually all the residue will dissolve except light flocculent silica; if not, the evaporation is again repeated. The silica is now filtered and weighed, and the result added to the weight of the silica in (1). A little zinc is dropped into the filtrate, and when dissolved, the ferrous sulfate is titrated by standard permanganate (page 229) diluted with nine volumes of water. The iron is calculated to ferric oxide and with the silica, subtracted from the weight of (2), giving the alumina by difference.

4. Manganous oxide. The united filtrates from (2) is acidified with five Cc. of glacial acetic acid, allowed to cool completely, and colored yellow with bromine water. Ammonia is then added till alkaline and the solution heated to boiling. The precipitated manganic hydrate (if any) is filtered and washed

with hot water, and purified from calcium by redissolving in hydrochloric acid and reprecipitating as before. It is calcined at a bright red heat in a platinum crucible, and weighed as Mn_3O_4.

5. Calcium oxide. First method. The united filtrates from (4) is concentrated to about 200 Cc. and precipitated by ammonium oxalate and ammonia. When the liquid clears, which requires some hours, it is decanted through a close filter and washed with hot water. The filter inclosing the precipitate is burned and the calcium compound ignited, at first gently, finally for one-half hour at a bright red heat. Weigh quickly and repeat the ignition until no further loss (greater than one milligram) is sustained.

Second method. The solution is evaporated to about 20 Cc. and the calcium precipitated by about ten Cc. of dilute sulfuric acid. Fifty Cc. of alcohol is added and after standing in the cold for an hour or more, the liquid is filtered and the calcium sulfate washed by dilute alcohol until free from chlorides. The filter and precipitate are dried, the filter separated and burned in a platinum crucible, and the ash moistened with a few drops of water and a drop of dilute sulfuric acid to revert to sulfate any calcium sulfide formed, and dried on the water bath. The precipitate is transferred to the crucible, heated to redness, and weighed as $CaSO_4$.

6. Magnesium oxide. The filtrate from either of the above methods is concentrated to 100 Cc. or less and after cooling precipitated by an excess of sodium ammonium phosphate and about 20 Cc. of concentrated ammonia. After stirring for a few minutes, not touching the sides of the beaker with the glass rod, let stand for some hours that the supernatant liquid may become clear; filter and wash with dilute ammonia (one part concentrated ammonia to five parts of water). The filter with the precipitate inclosed is burned, the crucible heated to redness, and the precipitate weighed as $Mg_2P_2O_7$.

7. Alkalies. Mix one gram of the mineral in a mortar with five grams of calcium carbonate and one-half gram of ammonium chloride. Transfer the mixture to a platinum crucible (if not large enough for the entire quantity, make two ignitions), and heat to redness for a half hour. Turn the sinter into a porcelain or wedgewood mortar and grind it to a coarse powder. Brush this into a beaker and *moisten* with water; when the lime has slaked to a soft paste, rinse the crucible and its cover with water into the beaker, stir well, and filter, washing with hot water. Precipitate the calcium from the filtrate by ammonium carbonate (page 207) and a drop of ammonium oxalate solution. When the calcium carbonate has become granular it is filtered and washed with cold water, and the filtrate tested for complete separation of calcium by a drop of ammonium oxalate. If it remains clear (or after filtration if cloudy), it is evaporated to dryness and the residue heated until all ammonium salts are driven off. The residue is dissolved in a little water and the solution filtered through a very small paper into a weighed crucible; a drop of hydrochloric acid is added and evaporated to dryness on the water bath. The residue is heated gently and weighed as $KCl + NaCl$; it should dissolve in water to a clear solution, except perhaps a trace of black carbonaceous matter practically negligible.

If the alkali chlorides are present in sufficient amount to admit of a practical separation — say in a quantity of over ten milligrams — the solution in dilute alcohol is precipitated by platinic chloride and the potassium platinchloride weighed, or the chloride determined and the bases calculated. If too small for separation the residue is reported as a mixture of the two alkalies, conventionally as $KNaCl_2$.

8. Combined water. Determined by igniting about one gram of the powder in a platinum crucible to bright redness, repeating to constant weight.

Calculation.

Fe_2	:	Fe_2O_3	: :	112.	:	160.
Mn_3O_4	:	$3MnO$	: :	229.	:	213.
$CaSO_4$	:	CaO	: :	136.17	:	56.1
$Mg_2P_2O_7$	:	$2MgO$	: :	222.60	:	80.6
$KNaCl$	:	$KNaO$	: :	133.06	:	78.16

Example. Weight taken for analysis, one gram.

Silica, etc., weighed .5054 gram. Less .0030 gram of residue, plus .0026 gram of silica recovered = .5050 gram. Silica = 50.50 per cent.

Alumina, ferric oxide, and silica together weighed .0056 gram. The silica weighed .0026, leaving alumina plus ferric oxide = .0030. Titration required 1.1 Cc. of permanganate of which one Cc. oxidized .0007 gram of iron; this gives iron .00077 gram = .0011 gram of ferric oxide. Ferric oxide = .11 per cent.

Alumina plus ferric oxide .0030; subtracting .0011 of ferric oxide leaves alumina .0019 gram. Alumina = .19 per cent.

Manganic oxide too small in amount to be weighed. Manganese oxide = trace.

Calcium oxide weighed .4750 gram. Calcium oxide = 47.50 per cent.

Magnesium pyrophosphate weighed .0055 gram. Magnesium oxide = .20 per cent.

Potassium sodium chloride weighed .0045 gram. Alkalies = .26 per cent.

Loss on ignition .0114 gram. Combined water = 1.14 per cent.

The analysis is then

Silica	50.50	Magnesium oxide	.20
Ferric oxide	.11	Alkalies	.26
Alumina	.19	Combined water	1.14
Manganese oxides	trace		
Calcium oxide	47.50	Total	99.90

The directions formulated for the separation of the bases apply to the analysis of silicates in general, with such modifications as the presence of other bases may necessitate, or a few changes where their proportion varies from those in the example given. Thus, should there be considerable ferric oxide or alumina it is best to precipitate them by the basic acetate process since the calcium and manganese are more perfectly separated than by ammonia. With much manganese it is preferable to dissolve the manganic oxide in hydrochloric acid and precipitate as ammonium manganese phosphate (page 243); etc. Silicates containing much alumina, or those associated with titanic acid present many difficulties for an accurate analysis.

B. Silicates insoluble in hydrochloric acid.

Quartz, glass, feldspar, mica, steatite, etc.

The general course of the analysis differs from the preceding mainly in that the silicate is made soluble by fluxing with sodium carbonate, the melt becoming double silicates of the bases and sodium, carbon dioxide escaping. Silicates containing lead (*e. g.*, table-glass) cannot be decomposed in this way since there is danger of metallic lead forming and alloying with the crucible — they are best dissolved in hydrofluoric acid and the silica found by difference.

One gram of the fine powder is mixed on glazed paper with about five grams of pure dry sodium carbonate, and the mixture turned into a capacious

platinum crucible and heated over a large Bunsen burner. When the fusion becomes tranquil the crucible is inclined, and after solidification, the lump dropped out into a large porcelain dish or casserole. The crucible is washed out and the lump digested with a large volume of hot water until entirely disintegrated. The dish is covered by a watch-glass and the liquid cautiously acidified by hydrochloric acid; the watch-glass is rinsed and the solution further proceeded with substantially as for a soluble silicate.*

For those desiring more extended practice in analysis selections may be made from the following, with especial attention to Numbers 1 to 6. Detailed directions will be found in the general treatises on quantitative analysis and in technical works on the special subjects, and need not be included here.

1. Elementary analysis of an organic or semi-organic body, *e. g.*, sugar, oxalic acid, an alkaloid, etc.
2. Gold or silver ore by the fire assay.
3. Sugar in cane or beet by the saccharimeter and Fehlings solution.
4. Natural water; industrial and sanitary analysis.
5. Fertilizer; for nitrogen, alkali and phosphoric acid.
6. Illuminating gas; complete analysis.
7. Soap; complete analysis.
8. Pig lead; complete analysis.
9. Iron ore; iron, phosphorus, silica, manganese.
10. Textile fabric; wool, cotton, silk.
11. Nickel matte; complete analysis.
12. Manganese ore; manganese and available oxygen.
13. Indigo; indigotin and indirubin.
14. Urine; urea, uric acid, and inorganic bases, and tests for albumin and sugar.
15. Licorice mass. (Analyst, 1898—94).
16. Meat extract. (Chem. News, 1890—1—290 and 303).
17. Creosote. (Amer. Journ. Pharm. 1899—409).
18. Opium; morphine.

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* References. Chem. News, 54—242; 60—14; 62—5; 69—171. Journ. Amer. Chem. Socy. 1889—421 and 1890—159. Crookes, Select Methods, 28. Fresenius Quant. Anal. 426.

PART 3.

SPECIAL AND TECHNICAL METHODS.

COLORIMETRY.

The practice of colorimetry has as a basis the principle that the depth of color conferred to a liquid by a chromogenous constituent body in solution, as viewed by transmitted white light, or the depth of color of a solid or powder viewed by reflected light, is in a direct ratio to the weight of the body in solution or admixture. In all the methods there is attained an equality of depth of color between the solution of the substance to be assayed and an arbitrary 'standard,' this usually a solution of the same or a similar chromogen as exists in the substance to be assayed.

The *depth* of color of a liquid or solid is the extent of the departure from pure white, while the *density* or tone of a given color is expressed by designating the various primary colors that unite to produce the given shade, and their relative proportions.* The two are independent, as the depth of any given color may vary indefinitely, and conversely, several different colors may be of equal depth. Colorimetric determinations are based on the depth of color, and are applied for the most part to solutions and liquids, less often to powders.

The plan of 'comparison by dilution' is usually adopted for occasional determinations, and is as follows: There is weighed of the substance to be assayed such an amount as will presumably yield a solution of a suitable depth of color for comparison, and of the pure colorific constituent or a compound thereof (the 'standard') as will produce a solution of approximately equal depth. After dissolving both in equal volumes of the solvent, the darker of the two is diluted with water or other colorless liquid until the depth is the same. The concentration of the solution of the sample is then deduced by a simple calculation from the volumes of the solutions and the weights of the sample and standard (page 183), the concentrations being inversely as the volumes. It is assumed, of course, that any colorific constituents of the sample other than the one determined have been removed or changed to some colorless combination before the comparison is made.

It is a fundamental rule of all accurate determinations that the two solutions shall be so made up that the relative concentrations as regards the chromogen shall be fairly equal before proceeding to dilute them. The reasons for this direction are (a) that generally the depth of color of a solution is not reduced in strict proportion to the dilution; and (b) the color itself is often modified by dilution. By preparing the solutions as directed, the error of (a) is kept within a negligible limit, and (b) the comparison of the depth of color is facilitated.

Other requisites are that both solutions be perfectly free from suspended matter and at the same temperature, and that the comparison tubes be of clear white glass and equal in bore, and uniformly illuminated by one source of light.

Usually a solid substance is prepared for comparison by treatment with a solvent and filtering, but it is not uncommon that a constituent that dissolves to a colorless or light colored solution may be oxidized, reduced, or otherwise chemically transformed to a highly colored combination. For example, a free acid in a liquid may on digestion with an insoluble hydroxide of a metal (*e. g.*, copper) dissolve an equivalent of the hydroxide to form a salt of a color suit-

* Journ. Socy. Dyers & Col. 1895—166.

able for comparison; or a base may be precipitated in combination with a colored acid radical (chromic, picric, permanganic), the precipitate filtered, redissolved and the colored solution compared with the corresponding chromate, etc. This scheme has an occasional use where certain associates of the constituent to be determined make other methods difficult of application.

Solutions of a hue unsuited for direct comparison can possibly be compounded with a suitably colored liquid that will reduce the hue to a comparable simple color. Thus, an aqueous extract of logwood when mixed with an ammoniacal solution of potassium chromate becomes of a pure blue.

The usual illuminant is diffused sunlight reflected from a dull white surface or transmitted through a ground or opal glass plate, tracing cloth, or other translucent white material. Of artificial lights, as a rule the whiter the flame the better, and the intensity should be ample to allow the tubes to be placed for comparison at a distance of several feet to be certain that the illumination is equal. Monochromatic light permits a sharper comparison of liquids of a compound color. For fluorescent solutions and those impossible to clarify, it is best to surround the tube with opaque material and arrange for the light to pass upward through the bottom.

In practice the two solutions are held in tubes of colorless glass, identical in bore and thickness of wall, and graduated in cubic centimeters and tenths. The tubes are either provided with glass stoppers, or the upper end beyond the graduation is bent to an angle of about 45° for convenience in mixing with the diluent. In order to cut off reflections from near by objects and shield the tubes from side-lights, the tubes may stand close together in a "camera" near the posterior end. The camera is a long shallow box of blackened wood, the anterior end open for viewing the tubes, and the posterior end closed by a sheet of white paper or opal glass illuminated by daylight or a monochromatic flame. Since the shade of a liquid when viewed in a round tube is deepest at the center, a flat tube or cell is preferable, or the modification of the camera shown in horzontal section in Fig. 143 — only narrow bands at the center of the tubes are seen, the remainder being screened by the wooden casing, A. To most observers the left hand tube appears the darker when the solutions are identical in depth of color, and the point of equality is known when either tube appears darker when at the left of the other.

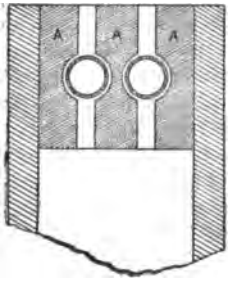

Fig. 143.

Where periodical tests are made of certain commercial raw materials or products in which the percentages of the coloring constituent vary only between narrow limits, a number of devices are in use to avoid the preparation of a standard for each test or batch of tests.

1. Of a sample containing the lowest percentage expected, there is dissolved a standard weight in a standard volume of solvent, in a test tube of standard diameter. A solution of a stable tinctorial body (as a salt of copper, iron, or cobalt, or an organic body like caramel or an aniline dye) is diluted or mixed with others in such ratios as will produce the same color and an equal tint when contained in a similar tube; the tube is hermetically sealed, and each sample to be tested, prepared as above, is diluted until identical to it in tint. As the colors of all these artificial standards fade in course of time, more quickly if organic, there has been proposed as a substitute colored glass rods, selecting from a series the proper diameter and shade for use. A few solutions act on the glass of the containing tubes and alter in shade by the constituents

dissolved, *e. g*, picric acid dissolving alkali from glass with a deepening in color.

2. The tentative dilution of the sample — at best a tedious operation — may be dispensed with by preparing a series of standards whose concentrations vary by regular intervals — say one-tenth of one per cent for the lighter and one per cent for the darker tints. A standard weight of each is dissolved and the series arranged progressively in a rack, Fig. 144, spaced to allow a similar tube containing the solution of the sample to be placed between any two. Across the back of the frame is stretched a sheet of white paper for a background. When the sample is placed between two of the tubes, being intermediate in tint, the eye can readily estimate the percentage to within one-fourth of the difference between the contiguous tubes. Or the series may be made up by diluting measured portions of the artificial liquid of (1) made of such a strength as corresponds to the highest percentage expected in the samples, with the calculated volumes of water or alcohol. The series is contained in sealed tubes, the rack shielded from the light when not in use.

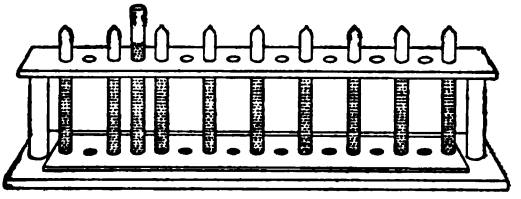

Fig. 144. 1/8

Following the general rule, a series made up of samples containing the chromogen in progressive ratios, will afford more accurate results than where one sample of a high percentage is diluted by the calculated volumes of water or other liquid.

Of certain commercial materials that contain varying amounts of a soluble adjective — a filler, make-weight, preservative, etc. — the series is best compounded of the pure chromogen plus corresponding inverse weights of the adjective. For example, in extract of logwood where the active principle haematein is associated with a mixture of one-third of chestnut extract and two-thirds treacle; the diluent of the standard should be a mixture in this proportion.

The 'tintometer' of Lovibond* is designed on strict scientific principles and is suited to a great variety of substances transmitting or reflecting colored light. The color-standards are thin glass plates of three pure colors, red, blue and yellow. A full set of each color comprises over 150 glasses, graded in degrees of depth of color. The intervals between the degrees are the smallest differences that the normal vision can differentiate; as the shades become lighter, and the ability to discriminate greater, the intervals are subdivided into tenths and hundredths.

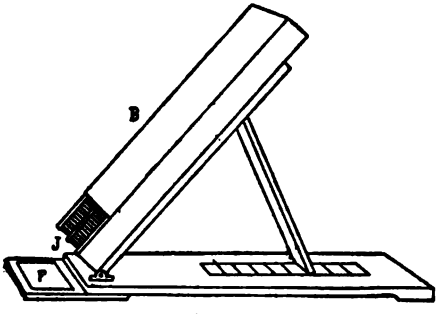

Fig. 145.

The standard of the system is the quantity of normal white light absorbed by the superposition of one red, blue, and yellow glass of unit depth. On

* Journ. Socy. Dyers & Col. 1887—186 and 1894—3, 22, and 206.

increasing the number of these combinations, the emergent white light grows dimmer and eventually is extinguished, and the luminous intensity of the light so absorbed is denoted by the number of combinations of glasses interposed. The standardizing is done by the maker against powders or definite solutions of pure chemical compounds.

The apparatus, Fig. 145, is a long narrow box B open at both ends and divided longitudinally by a thin partition. The box is supported at a convenient angle and points to a white reflector F, a layer of compressed precipitated calcium sulfate. On one side of the partition at J is placed a glass cell or bottle containing the liquid to be tested, and on the other side are superimposed such of the colored glass plates as will together transmit exactly the same hue and depth as the cell. From the sum of the plate numbers is determined the "visual composition." The dimension of the cell selected for a test is governed by the intensity of the color and shade of the inclosed liquid, ranging from one-eighth of an inch for dark liquids up to 24 inches for natural potable waters. Opaque bodies are illuminated by the same light as is reflected from F.

"The system of nomenclature is based on the fact that under ordinary daylight conditions, the vision is only simultaneously sensitive to two of the six colour rays which, when united, produce normal white light, the colour sensations of the remaining four being lost in what, for want of a better expression, we term the luminous intensity of the accompanying daylight. These two colours are always adjacent in the solar spectrum; for violet, the spectrum colours must here be considered as lying in a circle, the red and blue having violet between them." Red glass absorbs yellow, green and blue, and transmits violet, red and orange; blue glass absorbs red, orange and yellow, and transmits green, blue and violet; and yellow glass absorbs red, violet and blue, and transmits yellow, orange and green.

For example, a powder of commercial Prussian blue required standard glasses, viz., red 9.0, yellow 1.0, and blue 6.8. The yellow being numerically the smallest in the combination is taken to unite with 1.0 of red and 1.0 of blue to compose 1.0 of black. This leaves 8.0 of red and 5.8 of blue. Now, red glass absorbs blue rays, and blue glass red rays, while both transmit violet rays, here to the extent of 5.8; consequently the excess of red is $8.0 - 5.8 = 2.2$, and the visual composition is black 1.0, red 2.2 and violet 5.8.

The factors of a complex color sensation may be obtained by drawing three parallel horizontal lines of lengths corresponding to the unit values of the matching glasses, then drawing vertical lines through the termini of the two shorter. The three sections equal to the shortest of the horizontal lines represent the absolute chromatic units; the two interlinear sections, the monochromatic color developed; and the extension of the longest line, the proportion of the dominant ray.

Thus a five per cent solution of litmus required standard glasses to match, red 18.8, blue 21.2. The color sensation transmitted is therefore violet 18.8 + blue 2.4; for 18.8 units of violet is developed by the mutual absorption of 18.8 units of red and 18.8 of blue, leaving 2.4 units of unaltered blue.

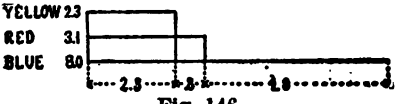

Fig. 146.

Again, a cloth dyed with a one per cent solution of Victoria blue matched 3.1 red + 2.3 yellow + 8.0 blue. From the diagram, Fig. 146, the color sensation transmitted is 2.3 black + .8 violet + 4.9 blue.

The tintometer finds use in dyeing and calico-printing, malting and brewing.

the manufacture of sugar and caramel; for the examination of oils, waxes and varnishes, the standardizing and comparing of pigments, flours, enamels, lards, etc., and for colorimetric determinations of carbon in steel, ammonia in potable water, etc.*

A variation of the usual practice of finding the point of equality in depth of color of two solutions is that of determining the thickness of a layer of a liquid of a complementary color that will extinguish the first. In this case a glass wedge is filled with a solution complementary to that in the sample tube and one beam of light is passed through both, the extinction point being shown when the wedge is in such a position that a neutral tint is transmitted, neither the color of the tube or that of the wedge predominating.

On this principle is the 'chromometer' of Koenig. He fluxes a minute weight of an ore, of copper for example, with a weighed amount of borax-glass in a small platinum cylinder, and views a ray of light passing through it and a wedge of amethyst glass which is complementary in color to the blue of the borax-bead. The wedge is made by grinding a narrow strip of body-glass to an edge at one end, and is mounted in a frame divided longitudinally into millimeters and moved transversely to the light-ray by a micrometer screw. The wedge is standardized by borax-beads containing known weights of copper.

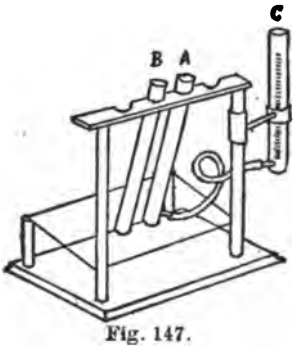

Fig. 147.

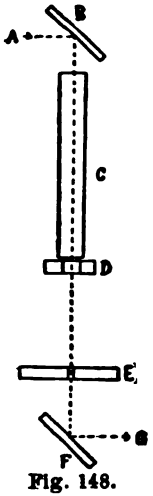

Fig. 148.

3. In dealing with liquids of a very light color a more satisfactory comparison can be made by viewing the tubes vertically instead of horizontally, the depth of color being greatly increased. Since dilution has here no direct effect on the depth of color, various arrangements have been devised for altering the heights of the liquids in the tubes at will. A simple plan is to provide the comparison tubes with taps situated near the bottom, and by drawing out part of the liquids alternately, equality in color-depth is finally secured. Another apparatus is shown in Fig. 147, the height of liquid in the tube A adjusted by raising and lowering a third tube C connected to A by rubber tubing.

In the Leeds color-comparator,† Fig. 148, the flat bottomed tubes C rest on a shelf D over a screen E provided with narrow longitudinal slits, one directly beneath each tube; daylight is reflected from the inclined mirror B down through the tubes to a second inclined mirror F on which appear images of the slits bearing the colors of the respective tubes. Or a fluid of the same color is inclosed in a long thin glass wedge resting on E,

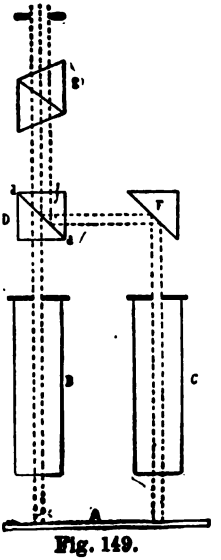

Fig. 149.

* Journ. Amer. Chem. Socy., 1896—269.
† Journ. Amer. Chem. Socy. 1895—301.

divided longitudinally into millimeters, the shade transmitted deepening uniformly as the wedge is moved from apex to base beneath a slit. The percentage corresponding to the shades at a division near each end of the wedge is found by comparison with samples previously analyzed, and the values of intermediate divisions interpolated.

In most colorimeters the images of the colors to be compared are separated to a greater or less distance, whereas a nuance is most evident when the two abut or at most are separated by a line only. This condition is obtained in some instruments by the aid of mirrors fixed at such angles that will reflect one image to the side of the other.

In the apparatus of Kruess, the principle illustrated in Fig. 149, refracting prisms are employed for the purpose. The liquids to be compared are held in two similar cylinders B and C, each covered by a hard rubber plate perforated at the center; light is reflected upward through the cylinders from a white porcelain plate A. The beam emerging from B enters a calcite prism D which has been cut diagonally and again cemented together at d d. The beam is polarized, the ordinary ray is reflected out of the field of vision by the plane d d, while the extraordinary ray proceeds into the Nicol prism E. The light emerging from the cylinder C meeting the prism F is also polarized, the extraordinary ray passing out, while the ordinary ray is reflected to d d and thence to E.

Entering E then, side by side, are the extraordinary ray from B and the ordinary ray from C. The Nicol E is so mounted that it can be rotated on a vertical axis and the angular deviation measured; as it is turned the apparent brightness of one ray increases and that of the other diminishes until at a certain position a one ray vanishes the other being at its maximum brightness, while at 90° from a the reverse is true. Midway between these two points the fields are equally clear, whether the cylinders are empty or filled with a colorless liquid or with equal volumes of a colored liquid.

But if the liquid in one cylinder is of a darker color than that in the other, the heights being the same, the angle of equal brightness will not be at 45° from a but at another angle as at ϕ, and if the positions of the cylinders be reversed, at ϕ'. Denoting the depths of color or concentrations of the solutions as c and c'; then

$$c : c' :: \tan \phi : \tan \phi'$$

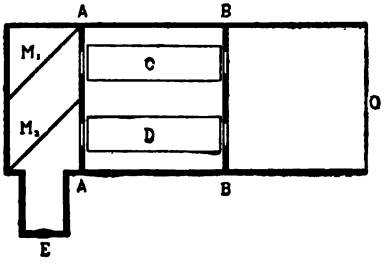

Fig. 150.

Proctor's colorimeter is shown in Fig. 150. A rectangular box open at O and facing a uniform light has two partitions AA and BB each with two orifices. In a line with these orifices are placed the glass cells C and D containing respectively the solutions of the sample and standard, or D may be one or more sheets of colored glass. M_1 and M_2 are two mirrors inclined to the longitudinal axis of the box at 45°, reflecting the pencils of light emerging from the orifices of AA to the eye-piece E. At the center of M_2 the amalgam is removed leaving a star-shape of clear glass: through this passes light reflected from M_1. If the depth of color in C is greater or less than in D, the eye will see through E a star darker or lighter than the field; when the depths are equal the star disappears.

The color-intensity of a solution or translucent solid can be expressed by the difference between the number of standard colored glass plates required to

extinguish a given light and the number required to extinguish the same light after emerging from a layer of standard thickness of the solution. The opacity of a solution due to finely divided suspended matter is measured by the depth of a layer of the solution which will conceal a white object.

Mills' chromometer, Fig. 151, is a glass jar graduated into 100 divisions, and is closed at the top by a metal cap which reaches to below the surface of the liquid. Through the cap slides, with easy friction, a glass rod B supporting at the bottom a white disk C. The jar is filled with the liquid to be tested and the rod depressed until the disk is just lost to sight, when the depth of the disk in the jar as read on the scale is the measure of the opacity of the liquid. This instrument is adapted to the determination of suspended precipitates or turbidities; where the suspended matter is white or of a light color, *e. g.*, the fat-globules of milk, a black disk replaces the white one.

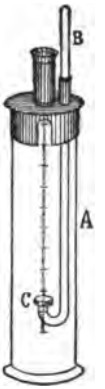

Fig. 151.

Hinds * measures the opacity produced by barium chloride in very dilute solutions of sulfates (*e. g.*, natural waters), by the extinction of a ray of transmitted light by the turbid solution. The apparatus is simply a flat-bottomed graduated test-tube held above a candle-flame; the turbid liquid is poured in until the image of the flame just disappears, viewing the tube axially. He finds that the product of the percentage of sulfuric acid by the depth of the liquid in centimeters is a constant, viz., .059, hence .059 divided by the depth of liquid equals the percentage of sulfuric acid in solution. In a similar way calcium chloride is precipitated by ammonium oxalate; here the product of the calcium oxalate by the depth of liquid is not a constant but of the form of a hyperbolic series. For such dilute solutions the method is claimed to be as exact as a volumetric one.

A similar scheme is applied by Vogel for the examination of albuminous urine. After acidifying the urine and boiling it to coagulate the albumin, the opacity is measured by noting the thickness of a layer that will cause the disappearance of the outline of a candle-flame. Oliver modifies the test by substituting for the candle-flame black lines of different widths ruled on white paper.

A modification of colorimetry, adapted to a compound which dissolves in water to a colorless solution but develops an intense color on contact with a reagent, is that of tentatively diluting the aqueous solution with water until a small definite volume withdrawn and mixed with the reagent shows no perceptible color when compared with water viewed under the same conditions. For a standard, a suitable weight of the pure compound is treated in the same manner.

The following examples may be of interest as illustrating the great variety of technical work to which the principles of colorimetry can be applied. From their simplicity and ease of manipulation, colorimetric methods are regarded with great favor by technical chemists for determinations that do not call for any high degree of accuracy.

A low-grade copper ore is quickly assayed by dissolving a fixed weight of the ore in a certain volume of nitric acid held in a test-tube. The solution is filtered and the clear blue liquid containing nitrate of copper is compared against a series made up of different weights of pure copper dissolved in nitric acid. Some operators prefer to deepen the colors by the addition of an excess of ammonia.

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* Journ. Amer. Chem. Socy. 1896—661.

Steel manufacturers follow the conversion of pig-iron to steel and grade the products by the aid of a similar scheme for determining the carbon contained. When steel drillings are dissolved in dilute nitric acid the carbon is oxidized to flocks of some compound of unknown composition which on heating dissolve to a greenish-brown solution. For a standard is taken a steel of about the same composition in which the carbon has been determined gravimetrically.

Paper is tested for wood fiber by moistening it with a solution of dimethyl-paraphenylene-diamine which has no action on cotton or linen but colors wood fiber red. As standards, papers containing known proportions of wood fiber are stained by the reagent.

The hydrogen sulfide evolved by the solution of a sulfide in a non-oxidizing acid, when brought in contact with a polished silver plate produces a tarnish of silver sulfide, which is yellow, brown, or blue, in proportion to the amount of gas impinging on the plate; or if the gas be passed through a cloth impregnated with a salt of cadmium there is developed a more or less deep yellow stain. This method is applied to some commercial metals that contain a minute amount of sulfide.

Wurstur determines the "active oxygen" in air (nitrous acid, ozone, etc.) by fastening a paper impregnated with tetramethyl-paraphenylene-diamine over the end of a glass tube .6 Mm. in bore, and drawing the air through by suction. Active oxygen in limited amount causes the paper to become blue. The color is compared with a scale of colors prepared by the action of iodine solutions of progressive concentrations on the 'tetra-paper.'

Pfeiffer determines the oxygen of coal-gas by passing the gas through an aqueous solution of pyrogallol. The standard is made by acting on cane-sugar by hydrochloric acid and adding the brown solution drop by drop to distilled water.

To determine the combined carbon of steel, Peipers,* paraphrasing the well-known touchstone test for gold alloys, would rub the steel on a white unglazed porcelain plate to abrade the metal, then treat the streak with a solution of copper ammonium chloride which dissolves the iron and manganese and leaves the carbon, the streak remaining more or less black according to the percentage of carbon in the steel. For comparison, steels of known percentages of carbon are similarly treated beside the sample.

Fritsche† proposes to determine the suspended carbonaceous matter in chimney-gas by drawing ten to twenty liters of the gas through a small glass filtering-tube loosely packed with cellulose. The cellulose is then transferred to a flask and shaken up with 200 Cc. of water to a uniform gray pulp. The pulp is compared with standards made by mixing .005 to .030 gram of soot with cellulose and treating as above. Permanent standards can be produced by washing cardboard disks with dilute india-ink.

Struve determines iodine in urine (coming from medicine exhibited) by mixing with fuming nitric acid and carbon disulfide, the former reagent liberating the iodine from its combinations, and the latter dissolving it with the acquirement of a violet hue. The standards are made up of different weights of potassium iodide dissolved in water and treated with the above reagents.

Rosanilin dyes added to red wine to heighten the color, are extracted by ether from the wine made alkaline by ammonia. A part of the ethereal solution is evaporated in contact with a thread of white wool of a certain size. The

* Zeits. angew. 1895—321 and 466; Stahl u. Eisen 1895—199.

† Zeits. anal. 1896—92.

colored thread is compared with a series of similar threads prepared from alcohol-ether solutions of magenta.

The yellow tone developed in an alkaline solution of mercuric iodide by traces of free ammonia is a valuable method for the determination of ammonia or its salts when in so dilute a solution that other methods cannot be applied.

The comparative money-values of several brands of a dye-stuff or dye-extract are approximately fixed by a colorimetric determination. Such weights as are inversely proportional to the vendors' prices are dissolved in equal volumes of a solvent, and it is noted with what additional volume each is to be diluted that it shall equal the lightest one taken as a standard.

Jean has proposed a method for the approximate determination of tannin in extracts of tanning materials, on the principle of the opacity of a precipitate. A beaker of a certain diameter is placed over a small disk of white paper lying on a black cloth. Into the beaker is poured a definite volume of weak standard solution of acidified ferric chloride. The aqueous extract of a certain weight of bark is then run in slowly from a burette until from the formation of green or blue iron tannate, the paper disk becomes invisible. Another experiment is made with a standard solution of the purest tannic acid obtainable, and from the relation between the two is calculated the percentage of tannin in the extract.

Blunt determines minute amounts of silver combined as nitrate or sulfate by dividing the solution into two equal parts; the first (*a*) is treated with a drop (an excess) of hydrochloric acid and filtered from the silver chloride. The filtrate and second portion (*b*) in equal sized beakers are placed before a black cloth; a drop of hydrochloric acid is added to (*b*), and to (*a*) small volumes of a weak standard solution of silver nitrate until the turbidities are the same. Double the weight of silver in the silver nitrate added during the titration is the weight of silver in the original solution. The above procedure nullifies the effect of any lead, etc., present in the original solution.

And generally, the color of many commercial articles or solutions is an indication, to a greater or less degree, of purity or the fitness of their application to some practical purpose. Examples are found in natural waters, beverages, edible, burning and lubricating oils, animal products, sugars, flours, etc., etc.

The color intensity of a pigment in powder is compared with that of an arbitrary standard by intimately mixing equal weights of each with a large proportion of a white powder such as china-clay. When the tints are identical, the weights of the diluent are in direct proportion to the tinctorial power of the pigments. The comparison of the standard and sample is done by laying a little pile of each adjacent on a sheet of matt-surfaced paper, white for the darker pigments, and black for the lighter. The piles are pressed down with a spatula, coming together with a sharp line of demarcation, and any difference can easily be seen.

Mills and Buchanan* propose a photometric method for expressing or determining the shades of a color. They proceed by dyeing equal-sized pieces of white cashmere in baths of the same dye of different concentrations. The pieces, now of graded tints, are arranged in rows on a vertical surface, and the whole covered with a cardboard perforated with circular holes of an equal diameter; there is exposed to view a circle of each of the dyed pieces.

Of this a photographic negative is taken, and a print is made on bromide of silver photographic paper. After 'fixing' the latter to dissolve out all unacted-on silver bromide, the disks are cut out, each incinerated and the silver in the ash determined volumetrically. The darker the shade of the

* Journ. Socy. Chem. Ind. 7—309.

cashmere, the more silver (reduced from silver bromide) is contained in the ash of the corresponding disk. Since one print would afford too little silver for an accurate determination, several prints are made and corresponding disks burnt together.

The observation of the color of a natural water is made on a column of not less than eight inches. For standards have been proposed Nesslerized ammonia solution, dilute solution of platinic chloride, Lovibond's plates, etc. Tidy recommends two hollow glass wedges filled respectively with a brown solution of a mixture of ferric and cobalt chlorides, and a blue solution of cupric sulfate, both of a definite concentration. On superimposing the wedges, a position will be found where the combination exactly matches in color and depth the water under examination. The wedges carry scales, each division indicating the breadth in millimeters at that point. The color of the water is reported to equal *a* divisions of the brown solution plus *b* divisions of the blue as viewed through a twenty-four inch tube. Various other isochromes have been proposed.

THE FIRE ASSAY.

Pyro-chemical methods are available for metalliferous ores, slags and mattes and some alloys, extracting the valuable constituent and leaving it in the metallic state in a pure or nearly pure condition and ready for weighing. They are applied to ores of gold, silver, platinum and allied metals, copper, tin, lead and iron, and to bullion, copper and lead mattes and speisses.

GOLD AND SILVER.

It is possible to determine the percentage of the precious metals in their ores by the usual gravimetric methods, but from the fact that ordinarily the metals or their mineral compounds are disseminated through a silicious or earthy gangue in extremely minute proportions, an inconveniently large weight of the ore would have to be operated on to extract even a weighable quantity of the metals, so that the fire-assay is found advantageous in the way of accuracy, economy, and time consumed.

The process comprises five stages.

1. Roasting — heating in a current of air to expel or oxidize certain elements in the gangue of the ore.

2. Crucible fusion or Scorification — collecting all the gold and silver into an alloy with metallic lead. The character and richness of the ore under consideration decides which of the two processes will be the most suitable for its assay.

3. Cupellation — oxidizing the lead of the alloy and absorbing the oxide in a cup of porous earth leaving a practically pure alloy of gold and silver.

4. Quartation — diluting the alloy from (3) with silver to assist in

5. Parting — dissolving the silver in nitric or sulfuric acid leaving the gold.

The roasting and quartation are often unnecessary and omitted.

On pulverizing some ores, particles of native gold or silver or their malleable minerals are flattened into disks. These are retained on the finer sieves and must be assayed separately, since they cannot be united with the powder with any assurance that the mixture is so homogeneous that it can safely be further subdivided down to the weight taken for the assay.

Crucible Fusion.

For the crucible process is weighed from one-fifth to two or more 'assay-tons' (page 41) of the powdered ore, the amount depending on the supposed content of gold or silver. The weighed amount is heated for some time to dull redness (roasted) with free access of air until no more fumes escape. The roasting is done in a shallow iron pan or clay dish coated with iron oxide to prevent the ore sticking to the dish. The roasted ore is mixed with various fluxes and carbon, and the whole turned into a large crucible made of fire-clay, Fig. 152. Over the surface of the charge is spread a layer of common salt, and the covered crucible is heated in a coke or gas furnace to a bright red heat until the charge and salt have come to a state of tranquil fusion. The crucible is allowed to cool until the melt has solidified, then broken and the small spheroid of lead containing the gold and silver of the ore freed from adhering slag and hammered into a cube for the process of cupellation. The reactions are

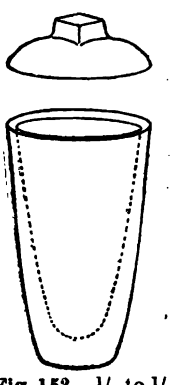

Fig. 152. $^1/_2$ to $^1/_8$

1. The roasting oxidizes or volatilizes elements like sulfur and arsenic which would interfere in the subsequent fusion. Powdered char-

coal is often mixed with the ore to transiently reduce some of the compounds of the volatile metals, which immediately afterward burn to oxides, the greater part passing off as fume. It is unnecessary to roast ores free from reducing elements or carbonaceous matter.

2. The general run of ores are made up of one or more of the commonly occurring minerals — quartz, silicates, calc-spar, dolomite, and the like, with more or less pyrite, galena, iron oxides, etc., and as a rule are infusible at ordinary furnace temperatures. But the silicates of lead and alkalies, and the double silicates of these and other bases (alumina, lime, magnesia, etc.) are easily melted. So the first step in an assay is to ascertain the approximate composition of the ore in hand, either by a qualitative examination or simply by inspection of the lumps; then to make up the charge of ore and fluxes of such a composition as will be fusible at redness to a mobile slag. If the gangue be principally quartz or the more silicious silicates, the fluxes are litharge (lead protoxide), sodium carbonate, and borax; if of the more basic silicates, some powdered silica is added to the above; while if decidedly basic in character (dolomite, hematite, manganese superoxides, etc.) the flux is largely made up of silica and litharge. The litharge should be free from gold, and the minute amount of silver present determined by a previous assay — it is seldom found entirely free from this element.

The silver in the ore is sometimes free (native silver) more often as chloride, sulfide, etc., but whatever the combination, metallic silver is produced either by reaction with an oxidizer (litharge), or a reducer (sodium carbonate or metallic lead) or by dissociation by heat alone. Gold is nearly always present in an ore in the elementary state, free or alloyed with silver, tellurium, or other metal.

3. Through the reaction with powdered carbon or a proportional weight of an organic compound, an equivalent of lead oxide is reduced to the metal, the lead being generated throughout the charge in the form of minute granules. The reaction between the silica of the ore and the sodium carbonate of the flux evolves carbon dioxide, which, as it escapes, causes a violent and protracted boiling of the semi-fluid mass. The particles of lead, gold, and silver are thereby brought into contact and readily alloy. Finally the effervescence ceases, the slag becomes a quiet mobile fluid, and the alloy sinks to the bottom of the crucible where the drops coalesce to one globule beneath the lighter slag.

From the equation $2PbO + C = 2Pb + CO_2$, it is easy to calculate what weight of carbon is to be admixed in the charge to give a convenient weight of lead (about 15 grams) for the subsequent cupellation. As many unoxidized elements that may be present in the ore will also reduce lead oxide, it is assumed that the ore contains none of these, or that they have been driven off or oxidized during the previous roasting. Some assayers invariably dispense with roasting, and instead make a preliminary test of the reducing power of the ore itself by melting an assay ton with an excess of litharge and the other fluxes. The weight of lead produced is subtracted from fifteen grams and enough carbon added in the assay to make up the difference; but if the ore should be so rich in reducing elements that the preliminary test gives more than fifteen grams of lead, carbon is omitted from the charge for the assay, and such a weight of niter is substituted as will reoxidize the excess of lead. Metallic iron, in the form of large nails, is often introduced in the charge, it combining with refractory pyrite to form easily fusible ferrous sulfide — $FeS_2 + Fe = 2FeS$.

In making up a charge, some assayers prefer to omit the oxidizer entirely and diminish the quantity of litharge to such an amount as will yield on reduction the proper weight of lead for cupellation, but as there is always left undecomposed more or less of the minerals of a reducing tendency — sulfides, arsenides,

etc., — there is room for suspicion that some of the gold and silver may be retained therein.

The layer of common salt melts and floats above the slag. It has no chemical functions, serving only to protect the charge against reducing gases from the furnace and to wash down any slag thrown up against the sides of the crucible.

The following is a well-tried general formula for ores that either contain no reducing constituents or have been previously roasted. The proportion of silica is to be varied according to the acid or basic nature of the ore under examination.

Ore	One assay-ton (29.167 grams).
Litharge	60 grams.
Sodium carbonate	30 grams.
Powdered silica	20 grams.
Anhydrous borax	10 grams.
Pulverized sugar	1 gram.
Salt to cover.	

Where it is known that a gold ore contains little or no silver it is the custom to add to the charge a small amount of metallic silver in the shape of foil, the object being to assist in collecting the gold during fusion and dispense with the operation of quartation.

Scorification.

In this process the unroasted ore is mixed with metallic lead and a trifle of borax and strongly heated for some time with free access of air. The ore floating on the surface of the melted lead is roasted to some extent, while the lead is continually being oxidized by the air passing over it. A part of the lead oxide transfers its oxygen to any antimony, arsenic, copper, etc., that may be in the ore, and these oxides, together with the borax and the silica and bases of the gangue combine with the remainder of the fluid lead oxide or dissolve in it, forming a complex, easily fusible slag of silico-borates of the various bases, while the gold and silver alloy with the unoxidized lead. Finally when the major portion of the lead has been converted to oxide, what remains is detached from the slag for cupellation, or a rescorification if necessary.

Fig. 153. $^1/_1 - ^1/_5$

The scorification is done in a small dish of baked fire-clay, Fig. 153, termed a "*scorifier*", and as the success of the operation depends primarily on an ample supply of air to oxidize the lead, it is heated by radiation from the walls of an incandescent *muffle*, Fig. 154; this is a thin semi-cylinder of hard-burned fire-clay, open in front, but closed at the rear where a narrow slit or small hole provides a vent for the fumes arising from the scorifier and creates a current of air through the muffle. It is supported horizontally in a special muffle-furnace, Fig. 155, made of clay or iron lined with fire-brick, and is surrounded with burning fuel, usually coke. For occasional assays, a smaller furnace heated by a gas blowpipe or gasoline burner will be found cleaner and more economical.

Fig. 154. $^1/_5 - ^1/_{15}$

The charge varies with the character of the gangue and is made up of from one-tenth to one-half an assay-ton of ore, five to fifteen times its weight of granulated lead (test-lead) and one-tenth to five-tenths gram of borax glass (anhydrous sodium biborate). Half of the lead is strewn over the bottom of the scorifier and covered with a mixture of the ore, borax, and the remainder

of the lead. The muffle being at a white heat, the scorifier is gradually moved back to the hottest part.

The lead melts at once to a globule with a convex surface; the air covers it with a film of oxide which immediately floats to the edge, again exposing a bright surface. In this way the oxidation goes on continuously until the size of the globule has been so far reduced that it disappears beneath the accumulated slag. This, of course, terminates the operation. The remaining lead and slag are poured out into a hemispherical or conical depression in a sheet of copper, Fig. 156, the lead sinking to the bottom. When cold the two are broken apart, and if the scorification has been successful the lead-button is malleable, and the slag homogeneous and free from undecomposed particles of ore. Frequently, however, the buttons from this or the crucible fusion are too large for cupellation, or they may be brittle from the presence of copper, sulfur, etc., and must be rescorified one or more times.

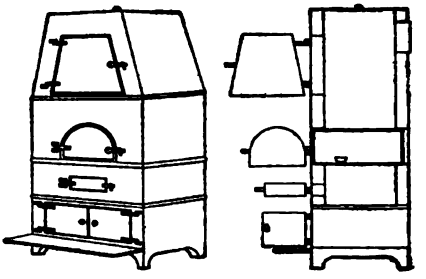

Fig. 155. 1/20

Of the two, the crucible process is best adapted for low-grade ores and tellurides, and those reasonably free from arsenic, antimony, zinc, etc. An objectionable feature of the crucible fusion is that the slag from some ores may be so viscid that particles of lead holding silver or gold may remain scattered through it, to be recovered only by a second fusion. It is seldom that a scorification-slag is too viscid, and if so can usually be thinned by proper additions. On the other hand, the small weight of ore that may be treated in a scorifier of moderate size (not over one-half an assay ton) limits the scorification process to the richer ores, though of course buttons from several scorifications can be united for cupellation.

Fig. 156. 1/4

From an ore containing much copper the lead button is found alloyed with metallic copper and cannot be directly cupelled. The copper can be oxidized and slagged off by repeated scorifications with lead. For cupriferous ores and auriferous copper mattes, a recent process* that combines the wet and dry methods has come into use. The sample is treated with moderately concentrated nitric acid, decomposing the sulfides, arsenides, etc., and dissolving all the metals except gold, tin, and antimony. A strong solution of lead acetate is added, followed by enough sulfuric acid to throw down a considerable precipitate of lead sulfate; this in falling envelops and carries down all the suspended gold, and on filtering, there is left in the paper a mixture of lead sulfate, insoluble silicates and silica, and any insoluble compounds of silver, but practically free from copper, arsenic, etc., and which can be scorified with ease. The filtrate is compounded with sodium bromide and sulfuric acid, precipitating the silver in solution and part of the lead as bromides, and the remainder of the lead as sulfate. The precipitate, also free from copper, etc., is filtered and scorified.

Cupellation.

This process is based on the resistance of the precious metals to oxidation by the air, even at high temperatures, and the ready oxidation of other metals.

* Journ. Anal. Appl Chem. 1892—262.

The *cupel*, Fig. 157, is a small cup made by compressing moist coarsely powdered bone ashes (calcium phosphate and carbonate) in a brass mold; after drying, it has a porous granular texture and absorbs liquids with great facility. It is heated in the muffle to bright redness to expel moisture and combined water and the clean lead button dropped in. The button melts and "clears" of the scum of oxide, after which the oxidation proceeds rapidly, most of the lead oxide being absorbed in the cupel, the remainder volatilizing. When all but a trace of lead is gone, the spheroid of gold and silver iridesces ("brightens", "fulgurates", or "blicks") from the refraction of light by the thin film of lead oxide enveloping it.

Fig. 157. $^1/_1$–$^1/_2$

Shortly after the iridescence the button solidifies, now practically free from lead.

Although it is presumed that silver is not oxidized in this process nor volatilized at the moderate temperature of cupellation, nevertheless so much may pass off as vapor or react with lead oxide and be absorbed in the cupel that a perceptible loss will be incurred. The minimum loss is sustained when the cupel is at such a heat that lead oxide fumes are just visible as they rise, so the assayer endeavors to maintain this temperature up to the point of iridescence, when it is raised to favor the removal of the last traces of lead. Tables of corrections for this loss may be found in works on assaying.

Alloys of gold, silver and copper, such as coins, bullion or jewelry, are wrapped in thin sheet lead and cupelled directly unless they contain too great a proportion of copper. A specific correction for cupellation loss is found by cupelling, side by side, the alloy and an equal weight of a "proof". The proof is made up from chemically pure gold, silver and copper in the same relative proportions as compose the alloy, this having been ascertained by a preliminary assay or volumetric determination of the silver and copper.

Quartation.

After weighing the button on an assay balance, the two metals are to be separated by dissolving the silver in an acid which will not affect the gold. The separation will not be complete unless the former predominates, so if a yellow tinge is perceptible in the alloy, there is incorporated with it by fusion on charcoal before the blowpipe, enough pure silver that the relative weights shall be at least two of silver to one of gold. The alloy is then rolled or hammered into foil and coiled into a spiral, and is ready for the operation of parting.

Parting.

The "cornet" is heated in a small flask with dilute nitric acid, the solution of silver nitrate poured off, and the residual gold washed several times with water by decantation. Finally the flask is filled with water, covered with a bisque clay dish, and inverted; when the gold has fallen through the water into the dish, the flask is cautiously removed. After the water has been absorbed by the clay, the gold is transferred to a platinum capsule, heated to redness and weighed. If the ratio of silver to gold has not been in excess of three or four parts to one, the gold is left in the form of a spongy mass with some coherence, but with a greater ratio, as a black powder. The washing and transference of the latter is more difficult to perform without mechanical loss. On heating to near redness, the black allotropic modification is transformed to the familiar yellow of the massive state, acquiring also a considerable degree of cohesion.

Volmetric methods.

The volumetric method of precipitation by sodium chloride is now universally adopted for the determination of silver in alloys on account of the greater accuracy and convenience as compared with the fire assay; the reaction is $AgNO_3 + NaCl = AgCl + NaNO_3$. Other reagents, such as sodium bromide, and barium chloride with zinc sulphate, have been proposed and certain advantages claimed, but sodium chloride still remains in common use.

The salt solutions are of two strengths—the standard (misnamed 'normal') containing 5.4207 grams of NaCl per liter of water at 15°, and a weaker one of one-tenth this concentration. Exactly one gram of silver is precipitated by 100 Cc. of the former, and 1 milligram by 1 Cc. of the latter. They are prepared by dissolving the above weight of salt in water and making up to one liter, then withdrawing 10 Cc. and diluting to 100 Cc. To accurately standardize them, one gram plus a few milligrams of fine silver is weighed and dissolved in nitric acid in a small flask and the solution cooled and diluted with water. One hundred Cc. of the stronger salt solution is run in from a pipette and the flask shaken until the precipitate has clotted, leaving the liquid clear. The small amount of silver remaining unprecipitated is determined by dropping in the decimal salt solution, shaking after each addition, until finally no opalescence is produced; here much is left to the expertness of the assayer in deciding the point where precipitation ceases.

From the volumes required for the test there can be calculated to what extent the stronger solution is to be fortified or weakened to be exactly standard; when this has been done, a portion is diluted with nine volumes of water to form the decimal solution. But since the strengths of the solutions vary slightly from day to day, from changes in temperature, evaporation, etc., it is customary to leave the concentrations unchanged and correct in the calculation for the variation from the strict standard.

In examining an alloy containing silver, a preliminary assay is made either by cupelling with lead, or by titrating a nitric solution by standard potassium sulfocyanide with ferric sulfate as indicator ($AgNO_3 + KCNS = AgCNS + KNO_3$, and $Fe_2(SO_4)_3 + 6KCNS = Fe_2(CNS)_6 + 3K_2SO_4$). Calculating from this datum, a weight of the alloy which will contain a few milligrams over one gram of silver is dissolved in dilute nitric acid and titrated as above by the standard and decimal solutions. Access of actinic light, which would reduce the silver chloride to subchloride, may be prevented by wrapping the flasks in black cloth or inserting them in pasteboard boxes, or by glazing the windows of the assay room with orange or red panes. No other metals present in alloys will interfere with the titration except mercury, and this is easily expelled by a previous fusion of the alloy or otherwise.

For the determination of silver in alloys where gold or platinum predominates, .500 gram is heated in a porcelain crucible with potassium cyanide and three grams of pure cadmium. When the metals have melted to an alloy the fusion is cooled, and the button, freed from adhering cyanide, is treated with dilute nitric acid; the silver, copper, and cadmium dissolve leaving the gold and platinum. The silver in solution is titrated by salt as above.

For the assay of gold bullion, samples are cut from the top and bottom of the ingot or bar. To a weight of .500 gram is added enough pure silver to make a ratio of two of silver to one of gold, and if no copper be already contained, a weight of .050 gram of pure copper which has the effect of toughening the silver button and insuring smooth edges on the cornet; the whole is wrapped up in a small sheet of lead. At the same time a 'proof' or 'witness' is made up from pure gold, silver, copper, and any other metals contained in the bullion, as nearly identical with it in proportions as possible, and a sheet of lead. The two are cupelled side by side in a hot muffle.

The buttons of alloyed gold, silver and copper are flattened under a hammer, annealed, rolled to foil, again annealed, and coiled into a cornet. The parting acid is nitric of about 1.27 sp. gr. in which the cornet is boiled for ten minutes; the container may be a test tube, porcelain crucible, or platinum cup. The boiling with acid is repeated to remove the last traces of silver and copper, and the residual gold washed, dried, annealed and weighed. Usually the weight of the gold from the proof is slightly higher, sometimes lower, than the original weight, and the assay is corrected accordingly.

Assay by the Blowpipe — Pyritology.

Assays accurate enough for prospecting and the exploitation of mines may be obtained by means of the mouth blowpipe. The process is essentially a reproduction in miniature of the furnace scorification and cupellation.

The charges for the blowpipe assay are made up about as follows.

	A.	B.	C.	D.	E.	F.
Ore (in fine powder)	.100	.100	.100	.100	.100	.100
Borax-glass	.050	.050	.050	.050	.050	.100
Sodium carbonate (anhydrous)	....	....	....	.050	....	....
Sulfur	....	....	....	....	.050	....
Lead (in powder)	.500	1.000	1.500	1.000	1.000	1.000

A is suitable for pure galenas whose gangue is not highly acid or basic; B, for general ore mixtures not highly acid or basic; C, for refractory sulfides, arsenopyrite, pyrite, copper sulfides, and ores containing much copper; D, for highly siliceous ores; E, for ores containing much iron; and F, for highly acid or basic ores.

1. Melting down. The charge is poured into a cylinder made by rolling a slip of paper around a pencil; the paper may be impregnated by sodium carbonate for the purpose of delaying combustion until the charge has melted down. The cylinder is put into a deep capsule made of carbon, the capsule resting in the end of a light holder. The paper is burned in the oxidizing flame of the blowpipe, then the charge heated in the reducing flame until the slag has become homogeneous and the lead has collected to one mass. The silver sulfide, sulfarsenide, and chloride that may be in the ore, here react with lead forming *e. g.*, lead sulfide and chloride, and arsenic sulfide, the silver alloying with lead.

2. The fusion is allowed to cool and the lead button detached. If the lead is dark in color or crystalline, it is to be refined by melting with borax in the reducing flame, then heating in the oxidizing flame to remove, in great measure, the sulfur and antimony.

3. The lead button is cleaned from borax and scorified in a thin clay cup in the oxidizing flame. The oxidation is carried so far that only a small lead button remains.

4. A cupel is prepared by ramming finely powdered bone ash into a depression in an iron disk. The button is heated so that all the litharge is absorbed in the bone ash, until the brightening takes place or it no longer reduces in size.*

The button of silver finally obtained is too small for weighing, even on the assay balance, so that its weight is deduced from its macro-diameter, it having been proved that the volume of the oblate spheroids of gold and silver of this minute size bear practically constant ratios to the volumes of spheres of the same transverse diameter. The measuring is done on an ivory plate on which have been drawn two fine lines AB and AC diverging at such an angle that at a distance from A of six inches, B and C are exactly .04 inch apart. From A to BC is divided into 100 equal parts, the divisions marked with the corresponding weights of buttons. The button to be measured is moved up and down between the lines until at some one division they are tangential to its circumference.†

* Crookes, Select Methods, 355.

† Chem. News, 15–281; Journ. Amer. Chem. Socy. 1901—203.

Gold ores may be tested along the same lines, but unless very rich, must first be concentrated by washing away part of the gangue.

The blowpipe assay has also been proposed for ores of some of the common metals.*

ORES OF THE BASE METALS.

The principle of the assay of the ores of lead, tin, iron, etc., is simply that of reducing the metallic compound by melting the ore in a clay crucible with some reducing agent and a suitable flux, including a desulfurizer if the ore be a sulfide, and weighing the more or less pure metallic button produced. It is assumed, of course, that no other reducible metallic compound than the one sought is present in a weighable amount. The results are generally too low owing to volatilization of the reduced metal or its retention in the slag, though the impurities in the button may offset these losses to some extent.

The so-called 'dry' methods for the base metals are still given the preference by some of the older metallurgists, one reason assigned being that as the methods follow to some extent the practice of smelting and refining, the results will indicate the returns that may be expected from the latter when carried on under favorable circumstances. The fallacy of this position appears when it is considered that the losses in the ordinary fire-assay are never so constant as in a well regulated metallurgical process, and there is not afforded the opportunity for comparing the merits of one practice against another, or of variations in the detail of the routine of any one. And so while the time-honored principles of the fire-assay are yet almost universally retained for the ores of gold and silver in default of better processes, for other metals, with few exceptions, the 'wet' gravimetric and volumetric methods have supplanted the 'dry' methods until the latter possess little more than a historical interest.

For the assay of *lead*, *antimony*, *bismuth* or *tin*† ores, potassium cyanide, at once a reducer, desulfurizer, and flux for the gangue, is the most satisfactory reagent; others are mixtures of sodium carbonate, borax, potassium bitartrate, flour, etc., with the addition of iron wire where the ore is a sulfide, and of hematite or cryolite to fix the silica of a tin ore. A layer of salt covers the charge. The closed crucible is rapidly heated to above the fusing point of the metal and the heat maintained until the reduction is supposed to be complete and the slag become fluid and hemogeneous. The contents of the crucible are then poured out into a mold, or the crucible is cooled and broken open, and the metallic button cleaned from slag and weighed.

To ores of *iron* are added silica, kaolin, or calcite according to the composition and acid or basic nature of the accompanying minerals. The viscous slag yielded by titaniferous ores is best thinned by fluorite. The charge is melted in a clay crucible thickly lined with a carbonaceous material (brasque) to remove the oxygen from the iron oxides. After luting on the crucible cover, the crucible is exposed to the highest heat of the furnace. The resulting button has approximately the composition of cast iron, and its hardness, tenacity, and the color and appearance of its surface and fracture, influenced by the various impurities present, are believed to foretell the quality of pig iron that the ore would yield if smelted in a blast furnace.

Copper ores (mainly sulfides, sulfarsenides and carbonates) are first roasted with charcoal to burn out sulfur and arsenic, assisted by an admixture with hematite, then with ammonium carbonate to decompose cupric sulfate. The roasted ore is mixed with argol, flour and sodium carbonate, or a similar flux, and the charge melted and poured into a mold. The copper button is generally too impure for direct weighing and must be refined by melting in a clay

* Fletcher, Quantitative Assaying with the Blowpipe.

† School of Mines Quart. 1892—368.

dish with borax-glass. The results of the assay are always too low from loss of copper in the slag.

Nickel ores contain sulfur, arsenic, cobalt, copper, iron, etc. Since nickel is infusible at furnace temperatures, it is combined with arsenic and weighed as nickel arsenide (Ni_4As_2), fusible at a bright red heat. The process is to roast the ore, first alone, then with charcoal, and finally with ammonium carbonate. The resulting oxides are mixed with arsenic and a reducing flux and melted down, yielding a button of the arsenides of nickel, copper, cobalt and iron. The button is scorified with borax-glass; first the iron arsenide, then the cobalt arsenide oxidizes and the products pass into the slag. The remaining button is weighed; if there was no copper in the ore it is nickel arsenide only, from which the nickel can be calculated, but if the ore contained copper, the button is a mixture of copper and nickel arsenides. In this case it is melted with a weighed amount of pure gold, and scorified with lead and ammonium sodium phosphate, all the arsenic and nickel oxidizing and passing into the slag. The remaining button is an alloy of copper and gold; it is weighed and the weight of the gold deducted, giving the weight of copper. The copper is calculated to copper arsenide, and knowing the weight of the copper-nickel arsenide, the nickel arsenide is found by subtraction, and the weight of the nickel calculated therefrom.

Native *platinum*, with the commonly associated minerals and metals—osmium, iridium, etc.—is pulverized and sifted. The siftings are mostly the sand of the ore with a part of the metals and are assayed in about the same way as an ore of silver, beginning with a crucible fusion. On the sieve remain most of the metals ready to be scorified with lead and cupelled, the platinum metals, like gold, alloying with lead and resisting oxidization. The buttons from the cupellations are unfused, spongy masses, containing considerable lead, and must be purified in the wet way or by re-cupellation with a weighed amount of silver. The buttons are then dissolved in aqua regia and the platinum metals separated from one another by fractional precipitation or otherwise.*

All the ores of *mercury* are decomposed on ignition with a carbonaceous compound, lime, or iron, with the liberation of mercury. The ore is mixed with one of the above and heated in a glass retort and the volatilized mercury received in cold water. When the distillation is finished, the water is decanted, the mercury dried on filter paper and weighed. For the poorer ores it is advised to extract the mercury with aqua regia, evaporate to dryness, and distill the residue. Amalgams and fouled mercury are distilled without any addition.

In the method of Eschka†, the edge of a deep porcelain crucible is ground to fit tightly against the under side of a shallow gold dish of slightly greater diameter. The ore is mixed with half its weight of clean iron filings, placed in the crucible, and covered with a layer of filings; the gold dish is weighed, filled with cold water and laid on the crucible. The vapor of the mercury, liberated on heating, condenses and forms an amalgam with the gold. The dish is emptied, rinsed with alcohol, dried at a low heat and reweighed—the increase is mercury.

The available *sulfur* in impure native thion or in pyrite may be determined by mixing the powdered ore with sand to prevent fusion, and subliming. For native sulfur the heat need only be moderate, but for pyrite should be considerably higher.

The *carbon* in a fuel may be estimated by mixing the powdered coal with a large excess of lead protoxide, pouring into a tube of refractory glass, and heating to above the melting point of lead. An equivalent of lead is assumed to be formed by the oxidation of the carbon; actually the method is only a measure of *all* the reducing matter in the sample.

* Crookes, Select Methods, 446.

† Trans. Amer. Inst. Mining Engrs. 28—444.

ELECTROLYSIS.

For the electrolytic determination of a metal, a current of electricity is passed through an aqueous solution of a combination of the metal with a suitable acid radical, by means of electrodes, usually of platinum. When the conditions of current strength, character of the electrolyte, superficial area of the electrodes, and temperature of the solution are within certain limits, the metal, slowly but completely, deposits on the cathode as a film closely adherent to the electrode. The increase in weight of the cathode is that of the metal deposited thereon.

The theory of electrolysis propounded by Grotthus in 1805 asserted that the radicals of the metallic compound are oppositely electrified, and during the passage of the current arrange themselves in lines with their similar ends in one direction, and are then disrupt by the electrical attraction of the electrodes. This simple hypothesis assumed the integrity of all the molecules and their symmetrical arrangement; it is no longer held.

Of modern theories and their variations no one can be said to be unassailable or to have gained entire acquiescence.* One of these is substantially as follows.

When an electrolyte (a compound that conducts electricity) is dissolved in water it separates into ions more or less completely according to its nature and the concentration of the solution. These ions, equal in number, are charged with like amounts of electricity, the cathions (metals) with positive, and the anions with negative. Under the influence of the electric current equal quantities of positive and negative electricity leave the solution, and the cathion ions, bereft of their electric charges, unite to form molecules; similarly an equal number of anion ions unite to form molecules. Moreover there is an actual migration or travel of the ions toward their respective electrodes, the cathions toward the cathode (negative electrode) and the anions toward the anode (positive electrode).

Under the influence of the current the electrolyte may undergo one of three changes.†

1. The ions may be transformed into others charged with different amounts of electricity to those formerly held, effecting under suitable conditions, the phenomena commonly known an oxidation and reduction. Thus, a mercuric salt is changed to a mercurous, and a ferrous to a ferric salt.

2. The anode being of the same oxidizable metal as that of the electrolyte, the cathions integrate at the cathode, while the anions do not leave the ionic condition for the reason that an equal weight of the anode to that of the molecularized cathions passes into solution as cathions, in this manner preserving the electrical balance of the system. As an example, witness the process of electrotyping, the electrolyte a saturated acidified solution of copper sulfate, the cathode of graphite and the anode of sheet copper; while the current passes, metallic copper is deposited on the cathode, but simultaneously an exactly equal weight of copper leaves the anode becoming copper ions.

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* Meyer, Modern Theories of Chemistry, 546 *et seq.*

† Journ. Franklin Inst. 1901—201.

3. Where the anode is a platinoid metal, graphite, or the like, it does not dissolve as in (2), but both cathions and anions become molecular, the former depositing on the cathode, and the latter either escaping as a gas at the anode or reacting with the solvent; thus cupric sulfate —

$$CuSO_4 + CuSO_4 + 2H_2O = Cu_2 + 2H_2SO_4 + O_2.$$

The possibility of precipitating a metal from its solution is a matter governed by the difference of electric potential between the metal and its possible electrolytes, and the density of current that is available. To a certain extent the density must be increased in proportion to the place of the metal in the electro-chemical series, the most positive, potassium, and several following requiring a current far beyond that ordinarily at the command of the chemist. In general, when the current density reaches a limit sufficient under the conditions of the experiment to electrolyze the solvent, hydrogen, and not the metal, appears at the cathode.

The source of electricity may be either a galvanic battery, a thermopile, a dynamo, or a storage battery. Until recent years the first named was invariably employed, it having the advantages of portability and low first cost.

For electrolytic work a choice of several forms of battery is allowed. All are constituted of two plates of dissimilar metals, or a metal and carbon, immersed in a suitable electrolyte. In some forms both plates are in one solution, in others there are two solutions, one plate in each, separated by a porous diaphragm, usually an unglazed clay cup. Elements with but one liquid are liable to weakening by polarization — the initiation of a potential difference in the opposite direction from that of the normal current, due to the collection of hydrogen on the surface of the negative pole.

In trade parlance batteries are classified as "open-circuit" and "closed-circuit." The former are designed for such purposes as exact but a momentary or intermittent current, and if kept in excitation for a much longer period, rapidly weaken or 'run down.' The latter furnish a less intense though more constant current for many hours or days without recharging with fresh solutions, and are more suitable for electrolytic work.

The exciting fluid (or fluids) of every battery is so chosen as to exert practically no chemical action on the plates until the wires leading from them are brought into contact, directly or through a solution that is a conductor. While this contact is maintained the circuit is said to be 'closed.' The chemical action that generates the current is the dissolution of the electro-positive plate with evolution of hydrogen, the gas being either liberated at the surface of the plate or reacting with the solution. The varieties most in use are —

1. The Daniell cell. A bar of zinc whose surface has been converted to a zinc-mercury alloy by amalgamation, is held in a porous clay cup; outside the cup is a cylinder of sheet copper, the whole contained in a glass jar. The porous cup is filled with dilute sulfuric acid, and the glass jar with a saturated solution of copper sulfate. As the zinc plate is coated with zinc-amalgam it is not acted on by the sulfuric acid until the circuit is closed. Copper wires, attached by soldering or screw-clamps to the plates, lead to the electrodes, from the zinc to the cathode and from the copper to the anode. A cell of one-gallon capacity produces a very constant current of about 1.079 volts.

The above has been superseded by modifications known as the "Gravity", "Hill", "Callaud", etc., in which the porous cup is dispensed with. A zinc disk hangs horizontally near the top of the glass jar; a copper plate or rosette

rests on the bottom and is covered with crystals of copper sulfate. The jar is filled with water, and after standing for some hours, the circuit being closed, the liquid separates into two layers, a saturated solution of copper sulfate below, and a (specifically lighter) dilute solution of zinc sulfate above. When in operation the copper of the copper sulfate is deposited on the copper plate, while the sulfuryl dissolves an equivalent of zinc from the zinc plate. The copper sulfate is removed from time to time as it becomes exhausted.

2. Bunsen's cell. Inside the porous cup is a rod made of dense carbon (gas-coke) in concentrated nitric acid; outside is an amalgamated zinc cylinder in dilute sulfuric acid. More powerful than the Daniell, it has the drawbacks of giving off irritating fumes from the reduction of the nitric acid by hydrogen, and of early polarization. A modification called the "electropion" has the same elements but different exciting fluids, namely, chromic and sulfuric acids in the porous jar and water in the outer jar; the zinc need not be amalgamated.

3. Smee's cell is a single fluid battery formed of two plates of amalgamated zinc and between them a plate of platinum or platinized silver. The fluid is dilute sulfuric acid. It furnishes a fairly constant current of .65 volts for several hours.

4 The Edison-Lelande is a popular type for electrolysis, having the advantage of a solid depolarizing element. The elements are zinc and copper oxide in a concentrated solution of caustic potash covered with a thin layer of paraffin oil to prevent entrance of carbon dioxide and aqueous vapor. The electromotive force is about one volt and the internal resistance about .3 ohm for polar surfaces four inches square at a distance of 1.5 inch. The capacity is from 300 to 600 ampere-hours.

For occasional determinations of copper, nickel, etc., the electropion is perhaps the most convenient, and for routine work, two or three Edison-Lelande cells or three to six gravity cells, connected to suit the work in hand.

A storage battery or accumulator has two plates of lead in dilute sulfuric acid; when a current from a battery or dynamo is passed for a time through the couple the surface of one plate is changed from metallic lead ultimately to the binoxide. Succeeding this transformation, the cell is at such a potential as to generate a nearly constant current for many hours, the binoxide gradually passing to the state of sulfate. Smith states that he is able to secure a more constant and controllable current from a Julien pile than from any other source.

Thermo-electric piles are built up of a number of bars of an alloy, such as zinc-antimony, and iron, the two soldered together at one extremity. A number of these couples are grouped radially around a Bunsen burner whose heat generates a weak constant current. All are liable to derangement and are difficult to repair. The most practical form is said to be that designed by Gulcher* which is equivalent to two large Bunsen cells; the electromotive force is four volts, the current strength three amperes, and the internal resistance .65 ohm. The consumption of gas is about six cubic feet per hour.

Small dynamos suitably wound can now be purchased, and generate a constant and easily regulated current. They are suitable in places where a large number of determinations are made periodically and motive power is available.

Through the extension of electric lighting during recent years many have the opportunity to use the current from an incandescent light socket. Since the voltage is far too great for the purpose, a suitable resistance is interposed, easiest by means of a number of incandescent bulbs.†

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* Stillman, Engineering Chemistry, 7.

† Journ. Anal. Appl. Chem. 1892—129.

The standards of measurement of the electric current, omitting those in less frequent use, are, according to the common system:

The *ampere*, the unit of current strength, represented by the unvarying current that will dissociate a solution of silver nitrate, under certain specifications, with the deposition of .06708 gram of silver per minute, or of copper sulfate, depositing .01969 gram of copper per minute. An ampere also dissociates dilute sulfuric acid with the evolution of 10.436 Cc. of oxy-hydrogen gas per minute measured under normal conditions; and the volume of these gases liberated by a given current times .0958 gives the strength of the current in amperes.

The *volt* is the unit of potential difference, electromotive force, or tension. It is a force so great that when steadily applied to a conductor whose total resistance is one ohm will cause a current of one ampere to flow. It is represented by 1000/1434 of the electromotive force of Clark's standard voltaic cell at a temperature of 15°.

The *ohm* is the unit of resistance to the passage of the current and is equivalent to that of a column of mercury at zero Cent. one square millimeter in cross section and 1.063 meters long. The Siemens' unit, frequently used to express the resistance of solutions and of batteries, is the resistance of a column of mercury 100 Cm. long and one square Mm. in section, at zero Cent. The reciprocal of the ohm is the unit of conductivity.

The unit of current is the *coulomb*, the quantity of electricity transferred by a current of one ampere in one second.

The density of a current signifies the quantity of electricity per square decimeter of electrode, and is found by dividing the current strength by the surface of the electrode immersed in the electrolyte.

The description of the current suitable for an electrolytic determination should specify the ampere units per square centimeter of cathode surface and the units of voltage.*

Practically, electrolytic determinations in the laboratory are restricted to the deposition of metals from aqueous solutions. To secure the deposit of a compact, tenacious film suitable for weighing, and in a reasonable time, the amperage and voltage of the current employed for each electrolyte must be adjusted within certain specific limits. A specific minimum voltage is required for every electrolyte, while the amperage determines the character of the deposit, and if the two are not in the proper relation, the deposition may be incomplete or tardy, or the film brittle, sandy, or spongy from occluded gas. The proper current for each metal is found by experiment; in general, copper, cadmium, bismuth, etc., need only currents of low potential, while iron, nickel, zinc, etc., are more resisting.

The formula for calculating the current pressure required for the decomposition of an electrolyte is $Z = \frac{w}{n \times 23067}$, where Z is the decomposition pressure in volts; w the thermal modulus expressed as the gram-calories set free in the formation of the chemical compound referred to one gram of hydrogen as a unit; and n, the number of valencies dissolved by the current. For example, cadmium sulfate is decomposed to cadmium, oxygen and sulfur trioxide, $CdSO_4 = Cd.O.SO_3$; $n = 2$, and $w = 89500$, hence $Z = \frac{89500}{2 \times 23067} =$ 1.9 volts. In electrolytic determinations the pressure does not usually exceed four volts.

* Chem. News, 1891—2—83.

The amperage of any given type of battery is increased by enlarging the surface of the elements, which may be done either by increasing the size of the cell or by connecting two or more cells in 'parallel' or 'multiple arc,' that is, by joining the connecting wires of all the negative poles and of all the positive poles together. To raise the voltage (independent of the size of any given battery) the cells are connected 'in series,' that is, the positive pole of one cell with the negative pole of the cell adjoining; or a more powerful type of battery is substituted. Other combinations may be arranged by connecting the cells partly in parallel and partly in series, this arrangement being designated as 'multiple series.' High amperage is indicated when large weights of metal are to be deposited; high voltage when an electrolyte is difficult of decomposition.

Let e represent the electromotive force of a given cell; r, the internal resistance to the current; and n, the number of cells of the battery. Then for a battery of n cells arranged in parallel, the electromotive force would be e and the internal resistance $\frac{r}{n}$. On the other hand, if the cells are joined in series, the electromotive force is $n.e$, and the internal resistance $n.r$. If arranged in multiple series, each group of a elements in parallel has an electromotive force of e and internal resistance of $\frac{r}{a}$; so that in a collection of n such groups, the electromotive force is $n.e$, and the internal resistance is $\frac{n.r}{a}$.

The adjustment of a current to suit a particular electrolyte may be done by reducing one more powerful. A substitute for the ordinary resistance board is simply a long iron or nickel wire of small diameter stretched zigzag across a board. One end of the wire is connected to the cathode, and a brass clip to the zinc pole of the battery. The clip may be fixed at any point on the wire, thus introducing the desired resistance. Another plan is to fill a large glass tube with a saturated solution of zinc sulfate; each end of the tube is closed by a cork through which passes a metallic rod having a metallic plate fixed transversely to its inner end. In proportion to the distance apart of the disks is the resistance increased.

The current is measured in the usual way by the ammeter and voltmeter, or by measuring the volume of oxy-hydrogen gas liberated when the current is passed through dilute sulfuric acid. In all cases the electrolytic solution should be included in the circuit.

For electrodes a material is used that is a good conductor of electricity and is not acted on by the electrolyte or associates in the solution. As a cathode mercury allows the deposition of certain metals by restraining ionic hydrogen from becoming molecular as it would do on the surface of a solid electrode. Dense carbon and graphite have been advised for some electrolytic separations. But practically, smooth sheet platinum is almost without exception made the medium for both the cathode and anode, it being a fairly good conductor and can be cleaned from deposits by suitable acids. Previous to the deposition of gold or platinum, a thin film of silver is deposited on the cathode in order that aqua regia may be used for dissolving the gold or platinum deposit and not attack the platinum of the cathode.

The form of the electrodes depends somewhat on the concentration of the electrolytic solution and the nature of the metal to be deposited;

1. The cathode may be a platinum dish of a suitable capacity to contain the solution, resting on a coil of bright copper wire connected to the zinc of the battery. The anode is a circular platinum plate of say half the diameter of the dish, to whose center is welded a thick platinum wire. The plate is suspended a little above the bottom of the dish. During the deposition a stream of bubbles arises from the anode, but they are individually so small that there is no loss by projection of drops if the dish is fairly broad. Objections to this arrangement are that any solid matter separating from the solution during electrolysis, or dust that may enter, falls to the bottom and is inclosed in the deposit and weighed with it, and that there is greater evaporation from a dish than from a taller and narrower vessel and consequently a wider ring of the deposit exposed to oxidation by the air. In the case of metals whose peroxides are conductors and deposit on the anode, the plate is made the cathode and the dish the anode.

2. Two platinum crucibles or dishes may form the electrodes, the smaller being suspended within the larger and at such a distance from it as will accommodate the solution. The gas-bubbles arising from the anode, which may be either the inner or outer vessel as is most suitable, tend to keep the solution homogeneous. Electric connections are made to the outer crucible by coiling copper wire around it, and to the inner by a tightly fitting cork through which is passed a copper wire terminating in a flat coil at the bottom.

3. The anode is a small open cylinder of platinum foil, the cathode a larger cylinder, both welded to heavy platinum wires, Fig. 141. The cylinders may be either partly or wholly immersed in the solution. A narrow longitudinal slit in each allows a better opportunity for the continual mixing of the solution during the electrolysis.

4. The cathode is a truncated cone of sheet platinum, with or without perforations in the sides, the anode a conical coil of platinum wire hung within the cathode.

Whichever form be adopted, it is essential that evaporation be prevented as far as possible (to avoid exposing the edge of the deposit to the air), and that the surface of the cathode have so great an area that the metal is deposited in a thin film only.

Supports for the electrodes or their suspensions should afford an amply large surface of contact with the leading wires from the battery and also allow them to be easily and quickly disconnected. Where one current is used for the simultaneous precipitation of a number of like electrolytes, the cathode of one solution is connected to the anode of the one next adjoining, and the terminal wires to the battery.

As a rule an electrolysis proceeds normally when the solution is at the temperature of the laboratory, though there are a number that require that the solution be maintained near the boiling point — actual boiling is apt to loosen the deposit from the cathode. The conductivity of a solution generally increases with a rise of temperature; thus, in electrolyzing a solution of gold potassium cyanide, the cathode a platinum dish standing near a window in cold weather, the gold was deposited incompletely and only on the side of the dish furthest from the window. Yet some metals separate completely only in the cold.*

The concentration of the metal in a solution can usually vary within wide limits without impairing the condition of the deposit. A fair concentration is

* Journ. Anal. Chem. 1895—613.

one gram of metal in 200 Cc. of liquid. The weight of metal that can be deposited depends on the area of the cathode, as too thick a deposit is apt to be rough and less adherent than a thin film.

To the rule that the electrolyte shall be in a clear solution for deposition there are a few exceptions, namely where the electrolyte may be in the form of powder gradually dissolving as the current passes and the metal precipitates.

The presence in the solution of the electrolyte of other inorganic compounds that are not decomposed by a current of the strength employed, has, as a rule, no interfering effect. Certain organic bodies, however, may hinder or prevent the deposition of a metal or modify the usual behavior; for example, the copper commonly present in oil of cajupet appears on the positive pole as copper *oxide* when the oil is mixed with water and electrolyzed.

Of the different radicals with which a given metal may be combined, the most suitable are those which require but a moderate current for decomposition at ordinary temperatures. With some exceptions the simple salts of the metals are not well adapted for electrolysis, as a moderate current precipitates them but slowly or not at all. The deposition proceeds more rapidly and regularly with double salts, the consort an alkali metal. To change a simple to a double salt it is usually sufficient to add an excess of the proper alkali salt to the solution.

Following is a synopsis of the forms of combination most suitable for electrolytic deposition. Some metals can be thrown down with equal success from any of several combinations, others from but one or two. Special conditions not mentioned here must be observed for many depositions.

1. Comparatively few metals can be precipitated satisfactorily from combinations with an inorganic acid, and it must be remembered that though the solution be neutral at the beginning, yet as the electrolyte is decomposed by the current the free acid increases. The nitrates of copper, silver and mercury are decomposed satisfactorily provided but little free nitric acid be in the solution; in neutral solutions free from organic matter, the peroxides of lead, thallium, and manganese form on the anode; bismuth, silver and copper can be precipitated from sulfuric solutions; while hydrochloric acid is unfitted for metals other than tin, platinum and palladium.

2. Most of the metals are readily deposited when combined as double salts with the tartrates, acetates, oxalates, or formates of alkali metals. Those that can be combined with ammonium oxalate are the members of the zinc and copper groups, and some of the platinum group. Metallic oxalates are broken up by the current to the metal and carbon dioxide, or in the case of the more electropositive metals, into hydrogen and hydrocarbonate of the metal. For manganese potassium oxalate, the manganese separates as peroxide on the anode.

Iron with ammonium tartrate; zinc, cadmium, and uranium (the latter separating as peroxide) with sodium acetate and acetic acid; and zinc as formate, yield readily to the current. The decomposition products of these radicals are generally quite complex.

Some radicals or the excess of an organic salt have a specific influence toward protecting the metal from oxidation during deposition.

3. The double alkali cyanides of the copper, zinc, and antimony groups (except arsenic) readily separate under comparatively weak currents. (The cyanides of sodium and gold or silver are largely employed in electro-plating.) The double sulfocyanides of the iron group have much the same characteristics as those of the cyanides.

4. The double alkali sulfides of gold, antimony and mercury (soluble in potassium sulfide), and the sulfo-salts of antimony and tin are decomposed by a current of adequate strength.

5. A number of the metals may be combined with alkali phosphates; these are cadmium, bismuth, tin, the manganese group, and some of the platinum group. Brand* advises the combination with sodium pyrophosphate in conjunction with ammonium carbonate for various metals. He also states that such double salts of the metals as form peroxides behave electrolytically different from the salts hitherto examined.

6. Members of the silver and zinc groups are precipitated from ammoniacal solutions of their double ammonium sulfates.

It will be noticed from the above that in the majority of cases the combination of the metal is with a comparatively weak radical.

The time required for a complete deposition ranges from two or three to twelve hours or more, according to the concentration and character of the electrolyte, the power of the battery, temperature, etc. Usually in an assay no harm results from a longer transmission of the current provided that it be uninterrupted, and the circuit may be closed in the evening and allowed to continue over night if convenient.

The precipitation, as a rule, is more complete than that afforded by other gravimetric methods, yet it is seldom that when a delicate test is applied to the residual liquid, traces of the metal will not be shown. Where the most accurate results are aimed at, the liquid should be concentrated and the remaining metal determined, colorimetrically where possible.

That the metal has separated up to the limit required may be assured by applying any one of the delicate qualitative tests for the metal to a few drops of the solution, premising that the solvent is not of a nature to interfere with the reaction. Of a few metals the fading of the color of the solution marks the abstraction of the metal. Or if the solution is diluted somewhat without interrupting the current, so that an uncoated surface of platinum be brought into it, the non-appearance of a deposit within the space of an hour or so is proof that only a negligible quantity remains; but with metals of nearly the color of platinum the formation of a slight deposit is difficult to detect. In any event the entire solution should be tested after the removal of the electrodes.

In most cases when the electrolysis is finished, the cathode may be withdrawn, rinsed by quick immersion in a beaker of water, dried and weighed. But if the original solvent, or that formed by the electrolysis, is of a nature to readily act on the deposit, a slight re-solution might take place however expeditiously the rinsing was done, and the current must not be stopped until the solvent is displaced by water. Here the liquid is drawn off by a small glass syphon reaching to the bottom of the vessel, at the same time pouring in water, carefully to prevent much mixing. The cathode is then disconnected and rinsed as before.

Ordinarily the metal may be dried at a temperature of 100° or below, though some prefer to rinse with strong alcohol and after draining for a moment, to light and allow to burn out, leaving the cathode ready for weighing. Others would follow the alcohol with ether and allow spontaneous drying.

As the weight of the deposit is learned from the increase in weight of the cathode it is best to heat the latter to redness before the original weighing to burn off adhering organic matter, and care must be taken that particles of the platinum wire are not detached by friction of the binding-screw connecting with the wire from the battery. A few metals readily oxidize with increase of

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* Chem. News, 1890—1—2.

weight on exposure to the air and must be protected as far as possible — thallium, for example, oxidizes so easily that a method has been devised by Neumann in which a special apparatus is provided for dissolving the deposit in hydrochloric acid without exposure to the air, calculating the weight of the thallium from the volume of hydrogen evolved.

Wherever the deposit is to be weighed directly it is highly important that it should form in a dense and closely adhering film. In this shape oxidation occurs to a less extent, if at all, than if it were loose and spongy. Moreover it is more easily cleansed from the adhering solution, and there is not the danger from mechanical loss incident to one granular or flaky. This condition is to be secured by a proper regulation of the current and the concentration and temperature of the solution.

The deposit is accounted pure metal, and in the majority of determinations this assumption is warranted. Yet unquestionably the tendency of certain deposits formed in complex solutions to occlude other matter has not been given the attention it merits. Thus, iron when precipitated from a combination with an organic radical always contains some carbon; under some conditions copper occludes gases and small amounts of other metals that may be in the solution*; peroxides formed on the anode are prone to inclose compounds not removed by washing. It is in technical work rather than scientific that complex solutions are dealt with, and greater precautions as to current strength, temperature and the like are indicated.

To some extent the appearance of the deposit is an indication as to its purity, denoted by a uniform lustre and the color of the unpolished pure metal. Local discoloration points to oxidation, general, to the presence of impurities.

The deposit may be cleaned from the electrode by immersion in a suitable simple acid; if of gold, chlorine water will dissolve it, and if of platinum a digestion in hot aqua regia, the electrode being protected by a film of silver deposited previous to the electrolysis.

SEPARATION BY ELECTROLYSIS.

Methods for the separation of two metals in one solution may be classified as follows: —

1. One metal may be so electro-positive that only a current of extraordinary tension will effect its deposition; the other is to be combined with a suitable radical and deposited by a current of ordinary density.

2. Both metals being precipitable, they are combined with such a radical that there will be a considerable difference in potential, and the current is adjusted to a tension that will only suffice to decompose an electrolyte midway between them in potential. When the first metal has completely deposited, the cathode is withdrawn and replaced by another and the current raised to the tension required for the separation of the second.

When a current whose voltage is gradually increased is passed through a solution holding different metals, that metal having the smallest potential difference in relation to the solution separates first, and alone up to a certain minimum concentration in the solution. If the potential difference be kept constant for a time, this required concentration may be lowered until qualitative tests show practically no metal remaining. At a higher tension that metal with the next smaller potential difference separates, and so on through the series.

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* Chem. News, 1889—2—24.

In the separation of two metals the form of combination best suited to any given pair can only be found by experiment, as there seems to be no general rule by which can be determined what combination will give the best results. One of the following is usually selected: an acid solution of the nitrates or phosphates; double cyanides or sulfides; or acid or alkaline double sulfates, oxalates, tartrates, or citrates. In one of these combinations can one group of metals be separated from another, though each combination seems best fitted for a few special pairs.

3. Both metals being precipitable, they are thrown down successively under different conditions of temperature and strength of current. Thus, copper is deposited from a cold solution in ammonium oxalate by a weak current, but not iron; while iron deposits if the solution be hot and the current strong.

4. Both metals being precipitable, one may be changed in valence during the passage of the current to a state not decomposed by an ordinary voltage.

5. One metal forms a stable peroxide, the other not. Here the two may be deposited simultaneously, the former as peroxide on the anode, the latter in the metallic state on the cathode.

The part played by the decomposition products of the radical of the metallic salts or the excess of the associated compound may be of importance to a perfect separation, as the electrolysis of one of the metals may be hastened or retarded ad libitum, while that of the other metal is unchanged, or in some cases may form an insoluble compound and precipitate. Thus, free nitric acid is decomposed to nitrogen tetroxide (N_2O_4), ammonia, water, and oxygen (liberated at the anode); hydrochloric acid plus water, to hydrogen and oxides of chlorine; ammonium oxalate to hydrogen and ammonium bicarbonate; potassium oxalate to hydrogen and potassium hydrocarbonate; and various organic radicals to complex dissociation products.

Thus, if during the electrolysis of iron and manganese oxalates, the solution contain a large amount of ammonium oxalate and is kept hot, the iron deposits on the cathode, but the manganese remains in solution until the ammonium oxalate is nearly all dissociated; this behavior prevents the occlusion of some of the iron in the manganese dioxide as would happen were both metals precipitated concurrently. The nitrates with free nitric acid act similarly.

6. Both metals are precipitated on one cathode; it is removed and made the anode in another solution so chosen that (1), one of the metals only will be dissolved, either remaining in solution or again plating the cathode; (2), both metals dissolve, one remaining in solution, the other depositing on the cathode; or (3), both leave the anode, one depositing on the cathode, the other becoming an insoluble compound.

The deposition of an alloy — that is, of two metals simultaneously on one electrode — is not difficult when they are not far apart in the electro-chemical series, but in proportion as they diverge the current must be more carefully adjusted that it may not be so weak as to deposit mainly the more electro-negative metal, nor so strong as to favor the more electro-positive. By this course it is possible to separate two electrolytically similar metals from a dissimilar third.

For example, LeRoy* separates nickel and cobalt from iron by first preparing an ammonical solution of their ammonium sulfates, the iron being held in solution by ammonium citrate. The three are precipitated on a platinum cathode by a suitable current. The cathode is removed to a concentrated ammoniacal solution of ammonium sulfate, made the anode of the circuit, and

* Chem. News, 1891—1—194.

the current passed. The nickel and cobalt dissolve and are deposited on the cathode, while the iron dissolves and is precipitated by the ammonia as ferric hydrate.

A commercial metal containing metallic or other impurities may be made the anode of a circuit with a sheet of platinum for the cathode. With a suitable liquid and strength of current the metal dissolves, either remaining in solution or depositing on the cathode according to circumstances. Most or all of the various impurities remain insoluble, in the form of a powder or skeleton, and may be filtered from the liquid.

7. In addition to the above there are various methods designated by some as electrolytic separations, but which logically belong to other classes. Of such are the deposition of an alloy on the cathode with subsequent separation of the members by other than electrolytic means, *e. g.*, by volatilization of one metal by heating, and the deposition of two metals from individual solutions after a separation according to a gravimetric method.

Electrolytic separations are not employed to the extent that would appear from the number of methods that have been published. One not skilled in electro-chemical analysis finds considerable difficulty in adjusting the current strength to harmonize with the dissociation factors of the electrolytes, or in modifying the current or removing the electrode directly one metal has been entirely precipitated and before the dissociation of the other electrolyte begins. This, of course, does not refer to the numerous cases where the separation is practically identical with the method of determination of one metal and allows the same latitude as regards the general conduct.

Electrolytic methods as compared with other classes of gravimetric analysis are superior in that various inaccuracies inherent to the latter are not incurred; that once the apparatus is arranged, the operation proceeds to a close with but little attention; that the product is obtained ready for weighing; and that if the residual solution is to be further dealt with, there are introduced no reagents of doubtful purity, difficult of removal, or interfering in any way. Their accuracy in many cases fits them for refined scientific analyses of compounds of the heavy metals, and even for the determination of atomic weights.

In technical analyses of certain alloys, commercial metals, ores, mattes and slags, simple and reliable methods are provided of equal or greater accuracy than any others now in use. For copper ores and products electrolytic processes have largely supplanted all others, and this is true to some extent of nickel ores; but for other metals volumetric or gravimetric methods still obtain the preference.

The disposition of some writers to extend the field of electrolytic analysis beyond its legitimate boundaries must be deprecated. Many schemes for the analysis of naturally occurring and factored commercial articles by quasi-electrolytic methods have been devised and considerable ingenuity shown in their adaptation, but one at all versed in analysis can readily see their inferiority to other methods or their impracticability for the average laboratory. For a large proportion of the material met with in practical analysis electrolytic schemes offer no advantage whatever and are inferior as a whole to the usual methods.

THE METALS AND COMMON ACIDS.

The literature on the separation and determination of the above is so extensive that space will not permit of more than a mention of the methods best known and generally available. More than this is unnecessary since the student has easy access to several exhaustive works on the subject, notably the treatises of Fresenius, Menchutkin, Jagnaux, Carnot, and Crookes.

Solution.

Water dissolves the majority of the salts of the different metals, and the free acids and alkalies. For commercial salts a trace of free acid may be added to secure a clear solution.

Nitric acid dissolves all the metals except gold and the platinum group, and tin and antimony, which are converted to oxides. As a rule this acid is chosen as the solvent for commercial metals and alloys. With a few exceptions, sulfides also are readily decomposed by the moderately strong acid with the formation of sulfate and nitrate of the bases, and separation of free sulfur, but fuming nitric acid, or the ordinary acid in combination with some strong oxidizer, is preferable for the reason that all the separated sulfur is converted to sulfuric acid on protracted heating of the liquid.

What nitric acid is toward the metals — an almost universal solvent — is *hydrochloric acid* for the oxides, all but a few readily passing into solution. Where a choice is allowed hydrochloric is preferred to either nitric or sulfuric acid, for the reasons that the chlorides are generally freely soluble, the excess of acid is readily removed by evaporation, and that most precipitants can be applied directly to a hydrochloric solution. Most peroxides enter into solution as protochlorides when treated with hydrochloric acid and a reducer such as hydrogen peroxide.

Hot concentrated *sulfuric acid* converts, with evolution of sulfurous acid, a number of the metals to sulfates soluble on dilution with water, and is sometimes applied in the form of melted potassium or sodium pyrosulfate. Many native oxides and silicates, insoluble in other acids, yield to prolonged treatment with sulfuric. The dilute acid dissolves some of the metals (with quantitative evolution of hydrogen) though hydrochloric can nearly always be substituted with advantage.

Sodium hydrate solution dissolves aluminum and zinc and is sometimes used for the separation of these metals from other elements. Melted potassium hydrate will resolve some refractory oxides and other insoluble compounds, and has been applied in connection with a current of electricity for the oxidation of certain native sulfides.

Sodium carbonate fused with any of the numerous insoluble native and artificial silicates forms double silicates of the bases soluble in water or a dilute acid. Other fluxes of more limited application are sodium fluoride for silicates; sodium carbonate and sulfur, or sodium thiosulfate for metals and oxides of the arsenic group; various fusible metallic oxides, borax, boric acid, etc., for silicates; soda-lime for chrome iron ore, etc.

Special solvents are hydrofluoric acid for native silica and silicates, nitric

or hydrochloric acid in conjunction with bromine, potassium chlorate or a hypochlorite for metallic sulfides, hydrochloric or sulfuric acid with a reducing agent for peroxides, etc.

Determination.

The *hydrates* of the iron group, manganese, nickel, cobalt and copper and the oxides of titanium, zirconium and gallium are precipitated by the alkalies. In presence of a strong oxidizer, managanese and nickel come down as perhydrates, and with a reducing agent copper as cuprous oxide. Alumina is precipitated from a solution in potassium hydrate by heating with ammonium chloride.

The precipitates are usually flocculent and as a rule not easy to filter. Where a choice of alkali is allowed ammonia is preferable, since occluded ammonia salts are volatile on ignition. The precipitates of aluminum and chromium hydrates are especially difficult to wash, while the perhydrates and peroxides are more granular. Many organic and a few inorganic bodies interfere with precipitation and must have been previously removed.

The precipitates pass on ignition to the state of protoxide or sesquioxide; manganese becomes the tetroxide and titanium the dioxide. Ignited in hydrogen, some oxides are reduced to the metallic state.

During electrolysis a few metals are deposited on the anode in the form of peroxides.

Hydrogen peroxide readily parts with an atom of oxygen leaving a residue (water) neither acid nor basic. In general, in acid solutions the reagent reduces peroxides, while in alkaline solutions proto-salts are perduced; the products remain dissolved or precipitate, or if insoluble originally, retain the solid form or pass into solution according to the nature of the acid or alkali.

The barium group, manganese, lead and cadmium are precipitated as *carbonates* by an alkali carbonate; zinc and bismuth as basic carbonates; and copper from a hot solution as oxide. The precipitates are granular and easy to wash, and with the exception of barium and strontium carbonates, pass to the oxides on strong ignition.

The aluminum group, gallium and indium are precipitated from neutral solutions by barium carbonate, an equivalent of barium entering the solution. The reaction was formerly much used for separations, but at present other methods have the preference.

The silver, copper and arsenic groups are precipitated as *sulfides* from acid solutions by hydrogen sulfide; the iron and zinc groups from alkaline solutions by ammonium sulfide. In view of the extensive use of these reagents in qualitative analysis, it is surprising to the beginner to find how comparatively seldom they are employed in a quantitative way. The reasons are (1), the tendency of the sulfides to oxidize during filtration and washing and pass through the filter; (2), that frequently there is free sulfur admixed with the precipitate, and that on drying or ignition there are left indefinite mixtures of the sulfide with sulfate or oxide, so that the precipitate can only be weighed after special preparation to insure its being entirely of the assumed composition, or it must be redissolved and precipitated in some other combination; (3), the transmission of a gas through a liquid is not so convenient as the addition of a liquid reagent, and the separation of one metal from another can usually be done as completely and more conveniently by some other reagent.

The sulfides of gold, silver and platinum are converted to the metallic state on moderate ignition, but those of arsenic, antimony and mercury are volatile and must not be heated above 100°. Of most other metals there is left on ignition a definite crystalline or amorphous sulfide ready for weighing if the

precipitate has been mixed with free sulfur and ignited in an atmosphere of hydrogen. Many sulfides pass entirely to oxides on prolonged roasting in air.

Hydrogen sulfide is an energetic reducing agent, often used for the reduction of solutions of per-salts, though the separation of free sulfur necessitates an extra filtration.

The *sulfates* of lead and the barium group are pulverulent precipitates, all except barium sulfate requiring the addition of alcohol to the solution and wash water to lessen the loss due to their solubility in water. All can be ignited without decomposition.

A volatile acid radical combined with an alkali metal, magnesium, nickel, etc., is displaced by the sulfuric radical when the compound is evaporated with a slight excess of dilute sulfuric acid and the residue gently ignited, the protosulfate remaining.

The *chlorides* of silver, mercurosum and lead form heavy curdy or crystalline precipitates easy to wash, that of lead being less soluble in dilute alcohol than in water. Like sulfuric acid, hydrochloric may be used to replace a volatile acid radical combined with a metal, and the resulting protochloride weighed.

Conversion of a metallic compound to the *metal*. Many metals can be deposited electrolytically with the best results.

Gold, platinum, copper, antimony, tin, lead and silver are precipitated by metallic zinc from slightly acid solutions as metallic powders, and some insoluble compounds of these metals are completely decomposed. In special cases for zinc there is substituted cadmium, iron, aluminum or magnesium, which can be bought nearly pure in the shape of foil or wire. Although this method has been largely supplanted by electrolysis, yet it occasionally finds use, especially in separations, from its quickness and convenience.

Gold, silver and platinum compounds are decomposed to the metals by strong reducers, such as ferrous sulfate, oxalic acid, and some organic compounds; and mercury by the powerful reducer stannous chloride.

Compounds of bismuth, lead, tin, etc., are reduced to the metallic state by fusion with potassium cyanide or sodium formate, or ignition in hydrogen.

The *oxalates* of calcium, zirconium, cerium, lanthanum, and didymium are fine powders, generally highly insoluble. On ignition they pass through carbonates to oxides. A number of other oxalates are fairly insoluble in dilute alcohol and can be determined volumetrically by potassium permanganate.

The *chromates* of barium, bismuth and lead are precipitated by potassium chromate from a solution containing only a weak acid in the free state, preferably chromic acid. The precipitates may be dried and weighed, or the chromic radical determined volumetrically and the equivalent of metal found by calculation.

The *phosophates* of aluminum and calcium, and the ammonium phosophates of cadmium, manganese and zinc are practically insoluble in dilute ammonia; on ignition the latter pass to the pyrophosphates. As a precipitant the substitution of a pyrophosphate for a phosphate has been advised for a number of metals.

The *platinchlorides* of potassium, ammonium, thallium, cerium, rubidium and ruthenium are crystalline compounds insoluble in dilute alcohol to a greater or less degree, and may be dried without decomposition. An alternate method is to isolate and determine the platinum contained.

The *ferrocyanides* of copper, bismuth, cadmium and gallium, and the *iodides* of bismuth, thallium, palladium and lead are sufficiently insoluble for the purpose of separation, though other methods for determination of these metals are preferred as a rule.

Compounds of certain metals with weak acids in nearly neutral solutions are decomposed on boiling, with the separation of all the base as a basic compound; such as ferric and aluminic succinates, acetates, etc. The method is one for separation rather than determination.

Nitroso-beta-napthol precipitates several of the metals from an acetic solution and gives excellent results as a separant. It has not come into general use, however.

Various specific reagents afford accurate and convenient means for the separation and determination of certain metals. Such are a sulfocyanide for silver and copper, tartaric acid for potassium, caesium and rubidium; ammonium chloride in conjunction with alcohol for the platinum group; ammonia for uranium; a cyanide for silver; tungstic acid for barium and calcium; molybdic acid for barium and lead; gallic acid for antimonic compounds; etc.

Argentic nitrate precipitates the halogens and hydrosulfuric, phosphoric, arsenic, chromic, ferrocyanic, ferricyanic, sulfocyanic, and uric acids as silver compounds, and as a rule quite completely. Formic and a few other organic acids reduce silver nitrate in a hot aqueous solution to metallic silver.

Barium chloride is the most common precipitant for sulfuric acid and is sometimes used for phosphoric, chromic, selenic and silicofluoric acids. Barium hydrate is the usual precipitant for carbonic acid. *Calcium chloride* precipitates phosphoric, hydrofluoric, oxalic, tartaric and citric acids, and carbonic acid in alkaline solution.

Lead acetate precipitates arsenic, phosphoric, chromic, vanadic, hydrosulfuric, molybdic, citric and hydrofluoric acids. *Mercurous nitrate* precipitates molybdic, phosphoric and chromic acids.

Magnesic-ammonic chloride, molybdic acid, ferric hydrate, and *uranium nitrate* each react with phosphoric and arsenic acids to form insoluble compounds. The first named reagent is generally employed for a gravimetric determination, the others for separation only.

As with the metals, various specific reagents are available.

On the evaporation of acid solutions of silicic and tungstic acids to dryness, these bodies pass to a form insoluble in water and dilute mineral acids, and may be filtered, ignited, and weighed as anhydrous oxides.

Certain acid radicals can be determined gravimetrically only after conversion to a higher or lower form; such are a chlorate, reducible by zinc and sulfuric acid to a chloride; a thiosulfate or sulfite oxidized by bromine to a sulfate; a nitrite converted to a nitrate; etc. In mixtures of the various oxygen compounds of one acidogen element, the oxidation or reduction may be done by a volumetric solution.

Solid mixtures of a neutral salt with free acid can often be separated by washing out the acid by alcohol, alcohol-ether, or other solvent in which the salt is practically insoluble. Volatile acids are separated from fixed acids by distillation, usually to be repeated several times.

Volumetric methods.

Potassium permanganate has perhaps the widest range of application of any of the volumetric solutions. The lower compounds of iron, tin, antimony, copper, uranium, thallium, molybdenum, vanadium, titanium, and tellurium in acid solutions are raised to higher states of oxidation; while in an alkaline solution (or one at most but slightly acid), manganese passes to insoluble perhydrate.

Like the metals, nitrous acid is oxidized to nitric, ferrocyanic to ferricyanic, sulfocyanic to hydrocyanic, sulfurous to sulfuric, etc.

When finely divided, some metals, such as arsenic, tin and copper, and suboxides such as cuprous oxide, may be dissolved in ferric chloride and the resulting ferrous chloride titrated by permanganate. Similarly, certain sulfides when freshly precipitated are oxidized to sulfates on digestion with a ferric chloride solution, the reagent reduced to ferrous chloride. Conversely, nitric acid is reduced to nitric oxide by ferrous chloride, an equivalent of ferric chloride resulting.

Oxalic acid is oxidized by potassium permanganate to carbon dioxide and water. Since many of the metals form oxalates insoluble in dilute alcohol, they may be precipitated as oxalates in a dilute alcoholic solution, the precipitate filtered and decomposed by dilute sulfuric acid, the free oxalic radical titrated by permanganate, and the weight of the metal calculated. Metals admitting of this procedure are lead, zinc, calcium, nickel, cobalt, cadmium, bismuth, cerium, lanthanum, and didymium. A shorter method is to precipitate the metal by a known weight, a moderate excess, of oxalic acid or ammonium oxalate, and titrate the excess in an aliquot part of the filtrate.

A similar plan may be followed with a few metals using a ferrocyanide as the precipitant, this oxidized to ferricyanic acid on titration by permanganate.

Hydrogen peroxide in the form of a weak standard solution may be employed for direct titration, but is more often used as an adjunct to permanganate. Acting on the one hand as an oxidizer of protoxides or suboxides or a perducer of lower compounds or as a reducer of peroxides or per-salts, and on the other as a reducer of permanganate, many metals can be determined by back titration. However, methods based on the expulsion of the excess of hydrogen peroxide by moderately protracted ebullition of a solution are vitiated by the fact that a dilute aqueous solution of the peroxide may be boiled for a long time yet some peroxide remain dissolved.

Of the standard acids, *hydrochloric* and *nitric* are well adapted for determinations of the caustic alkalies and earths, their carbonates and bicarbonates; sulfuric and oxalic acids are not so suitable for the earths and earthy carbonates on account of the insolubility of the resulting compounds. As bases, the *alkali hydrates* are suited to the titration of the inorganic acids, and with proper indicators, to the organic acids. The earthy hydrates have a more limited use, since their carbonates are insoluble, as are their phosphates, sulfates and tartrates.

A number of the metals can be determined by an indirect volumetric process, given a neutral solution of a normal salt. The metal is precipitated as hydrate by an excess of standard alkali or alkali carbonate, and the excess of alkali titrated by a standard acid. Many haloid salts are decomposed on digestion with silver oxide, the reaction yielding an insoluble compound of silver and free base, the latter determinable by standard acid.

Free iodine is converted to hydriodic acid by many reducing agents. By standard *iodine* solution may be titrated thiosulfuric, hyposulfurous, sulfurous, arsenious, antimonious and hydrocyanic acids, using starch-paste as indicator.

Sodium thiosulfate is oxidized to the tetrathionate by free iodine. Any chemical compound that on distillation with hydrochloric acid yields chlorine quantitatively may be determined by passing the evolved chlorine into a solution of potassium iodide, then determining by standard solution of thiosulfate the iodine set free. Many peroxides and per-salts, the chromates and bichromates, iodates, chlorates, etc., may be analyzed in this way. Finely divided metals that unite directly with iodine, and sulfides that exchange an atom of sulfur

for one of iodine can be determined by a reverse titration, as well as a few compounds that decompose potassium iodide with absorption or liberation of iodine.

Potassium bichromate is a direct oxidizer like permanganate, though having fewer applications. That it is not decomposed by most varieties of organic matter in cold dilute solution is an advantage at times, as in the titration of inorganic bodies in presence of organic matter. The standard solution reacts with ferrous, stannous, and cuprous compounds, and arsenious, antimonious and nitrous acids. It may be used also as a volumetric precipitant for lead and a few other metals.

The haloid compounds of silver being quite insoluble, all soluble inorganic bodies containing a halogen can be titrated directly by *silver nitrate*, cessation of precipitation marking the end-point. Many carbonates, nitrates, and like salts can be converted to chlorides by repeated evaporation with hydrochloric acid, and the chlorates and perchlorates by nascent hydrogen, and the chloride titrated. Silver nitrate is also used for the titration of cyanides, sulfocyanides and soluble sulfides; ammonium silver nitrate for sulfides in presence of chlorine.

Sodium chloride (or *bromide*) forms with silver salts insoluble silver chloride (or bromide) and is the specific volumetric solution for this metal, though others are occasionally used. In connection with silver nitrate, it may be used in a reverse titration for the determination of the halogens combined with metals.

Oxalic acid or ammonium oxalate is sometimes used as a precipitant for lead and calcium, the end-point found by filtering a portion and testing by the titrand. Various peroxides and per-salts are reduced by oxalic acid, the determination made by a back titration with permanganate.

Stannous chloride reduces most peroxides and per-salts to the normal, and some normal salts to sub-compounds. Examples are ferric, chromic and manganic salts reduced to the normal, cupric salts to cuprous, and mercuric salts to mercurous and later to metallic mercury. The indicator for these titrations is usually ferric sulfocyanide, bleached by the slightest excess of the titrand.

Potassium and *sodium sulfides* precipitate many of the metals as normal sulfides and are chiefly used for copper and lead determinations. The end-point is found by spotting drops of the titrate on paper impregnated with a lead compound which shows a brown stain with the least excess of sulfide.

A number of reagents are applied for special determinations.

Colorimetric methods.

Comparatively few of the metals form compounds soluble in water of a color sufficiently deep for a colorimetric determination. Direct comparisons are possible with aqueous solutions of the salts of gold, platinum, copper and chromium, and the ammonium salts of copper, cobalt and nickel. Specific compounds of ferric and ferrous iron, chromium, manganese, lead, gold, platinum, vanadium, etc., possess a color suited to comparison. In all cases, the methods are best adapted to small proportions of the metal in a mixture, and where strict accuracy is not essential.

ELEMENTARY ORGANIC ANALYSIS.

A determination of the elements composing an organic or partly organic body is resorted to for the purpose of deducing an empirical formula, or to learn the proportions of the elements, or by calculation, the compounds of a mixture. In most cases there are to be determined carbon and hydrogen, frequently also oxygen and nitrogen, and sometimes sulfur, phosphorus, a halogen, etc.

The purity of an organic compound submitted to an ultimate analysis to learn its formula is always to be assured by appropriate tests. A commercial article, known to be more or less impure is usually analyzed without previous preparation beyond drying or the evaporation of an aqueous solution to dryness.

All the methods involve the destruction of the compound. Carbon and hydrogen are converted into carbon dioxide and water which are collected and weighed and the weights of the elements calculated; nitrogen is either isolated as a gas whose volume is measured, or converted, by assimilation of hydrogen, into ammonia to be determined gravimetrically or volumetrically; oxygen is almost invariably determined by difference; sulfur and phosphorus by oxidation to their respective acids and a gravimetric determination; and other elements by well known general or special methods, after destruction of the organic matter by oxidation.

CARBON AND HYDROGEN.

For the determination of these elements the organic substance is burned by oxygen furnished by some easily reduced metallic oxide or other compound, or in a current of oxygen or air, or both.

The simplest form of apparatus is that originated many years ago by Liebig and still in occasional use. The combustion is done in a tube A, Fig. 158, about 18 inches long and 1-2 inch in bore, made of a special refractory glass.

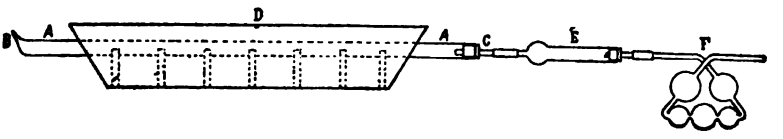

Fig. 158.

The tube is drawn out at one end to a narrow tail B which is sealed, the other end left open. It is charged for a few inches with granular cupric oxide, then with the organic body previously mixed with granular copper oxide, then to the end with copper oxide. The end is closed by a cork carrying a short glass tube C, and the tube laid on the supporting ridges of a chauffer D.

A light glass tube E, holding dry granular calcium chloride kept in place by plugs of cotton, is weighed and connected by a short piece of rubber tubing with C; a light absorption bulb F, partly filled with a strong solution of potassium hydrate, is also weighed and connected to E. It is ascertained that all the connections are air-tight, and the apparatus is in readiness for the combustion.

The charcoal in the chauffer is kindled a few inches back from the cork, and as the copper oxide becomes hot, the remainder of the tube is heated, grad-

ually approaching the tail. The organic compound first chars, then burns at the expense of the oxide in contact with it, the carbon becoming carbon dioxide, the hydrogen water, and the nitrogen escaping uncombined. The formation of gases in the tube and their expansion by heat drives them out through E and F. An indication of the presence of nitrogen in the organic body is that bubbles pass through the potash during the entire combustion, while, if absent, all the gas is absorbed toward the close of the operation.

The water from the combustion is retained in E by combination with the anhydrous calcium chloride, forming the hydrated compound $CaCl_2.6aq$. The carbon dioxide unites with the potassium hydrate in F to form potassium carbonate.

The combustion tube remains filled with gas after the combustion is ended, and to sweep this also through E and F the open end of F is connected by a rubber tube to an aspirator bottle, and over the tail of the combustion tube is slipped a rubber tube leading from a supply of purified and dried air. The end of the tail is broken off by nippers, and air drawn slowly through the apparatus until the gases in A have been swept out. E and F are weighed after cooling, and the increase over their previous weights are the respective weights of water and carbon dioxide they have taken up. The weights of carbon and hydrogen in the organic compound are calculated from these figures, observing that if any moisture, combined water, or carbonates decomposed by heat were in the compound, a deduction from the weights of water and carbon dioxide must be made accordingly; these corrections are deduced from separate tests.

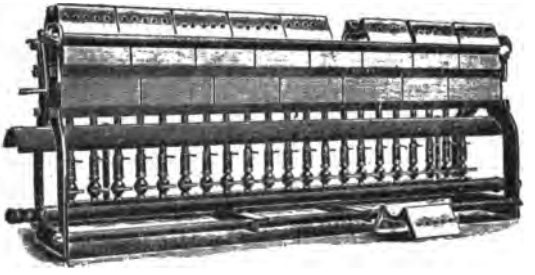

Fig. 159.

Certain defects in Liebig's apparatus are remedied in the modern furnace and train which differs in several particulars, though arranged on the same general plan.

1. The charcoal furnace has been superseded by one burning illuminating gas, Fig. 159. The combustion tube is supported above a row of Bunsen burners, each with a stopcock. Above, before and behind the tube, an inch or two distant, are movable plates of fireclay that serve to radiate the heat from the burners to the upper part of the tube and to protect it from draughts.

Fletcher's furnace, Fig. 160, is entirely of fireclay made in short sections that may be joined to accommodate any length of tube. A row of burners stands at the front of the furnace, inclined to throw the flames under the tube, entering at perforations in the front of the furnace.

Fig. 160.

Furnaces burning kerosene or gasoline have been designed for laboratories not provided with illuminating gas, but are not so convenient as the latter. For a platinum combustion tube no furnace is needed, a row of Bunsen burners supplying sufficient heat for the purpose.

2. A glass combustion tube, though it has the merit of allowing an observation of the prog-

ress of the combustion throughout the operation, can be heated only to dull redness, as above this point there is danger of the tube becoming softened and perforated by the pressure of the gases within; nor is it always easy to secure a highly refractory glass for the purpose. So that for bodies leaving a dense coke on heating, it is better to substitute a tube of another material.

A porcelain tube will bear a very high temperature, and with proper care in heating and cooling can be used for several combustions. The tube must be well glazed interiorly, and of a sufficient length to project far enough beyond the furnace that the corks or rubber stoppers closing the ends will never become heated to the point of charring.

A platinum tube is far superior, except as to opacity, to one of any other material; the cumbrous and expensive furnace, so unpleasant in hot weather, is not needed, and one escapes the frequent annoyance of a determination spoiled by the perforation or cracking of a glass or porcelain tube. Though the first cost is high, for routine work it is more than compensated by the durability — the author has made over a thousand combustions in a platinum tube without its appreciable injury. That platinum is permeable to gases when at a red heat has been shown to be of no significance in the ordinary combustion process.

The best form of tube is shown in Fig. 161; one end is contracted to a narrow prolong, and in the other end, reinforced by a German silver band, is inserted a hollow metal plug ground to fit gas-tight, and terminating in a narrow metal tube; but a cork and glass tube will answer the purpose quite as well or better.

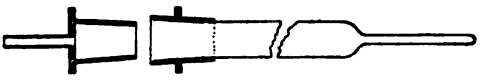

Fig. 161.

Schwartz proposes a tube of seamless copper, the corks at the ends being protected from conducted heat by water-cooled jackets, and Summers * arranges for a short platinum tube on the same plan. Shimer † still further reduces the cost of platinum apparatus by substituting for the tube a large platinum crucible closed by a water-jacketed stopper.

3. Instead of oxidizing the organic body by copper oxide, lead chromate, etc., alone, it is more prudent to transmit during the operation or near the close, a current of pure oxygen, finally replacing it by a stream of air. The oxygen and air are drawn from gasometers or gas-bags or from metal tanks, and before entering the combustion tube are purified by being passed through a solution of caustic potash to remove carbon dioxide, chlorine, etc., then through concentrated sulfuric acid to absorb moisture. It is said that oxygen compressed in metal cylinders sometimes contains gaseous hydrocarbons taken up from the oil used to lubricate the compressor, and that gases stored in rubber bags may also contain carbonaceous compounds; where this is suspected the gas is passed first through a short porcelain tube containing fibrous asbestos kept at a dull red heat, or through a capillary platinum tube heated to redness by a Bunsen burner, thence to the purifying tubes precedent to the combustion tube.

4. The organic body may be burned in oxygen alone, omitting any oxidizing reagent. A solid or semi-solid body is weighed in a porcelain or platinum boat, Fig. 162, and after the combustion the boat reweighed, it containing any fixed inorganic constituents of the substance. If the organic body is a liquid of high boiling point, the boat is filled with sand or powdered copper oxide and the liquid imbibed therein. A volatile liquid is weighed in a thin glass bulb with a capillary stem through which the liquid gradually exudes as the bulb

* Journ. Amer. Chem. Socy. 1896—1087.

† *Idem*, 1899—557.

becomes heated; or the bulb may be sealed up after filling, and eventually broken by the expansion of the liquid on heating. An extra long combustion tube is needed for volatile liquids, that the surface of hot copper oxide traversed by the gases may be ample to oxidize any organic vapor or carbon monoxide produced, and the tube must be heated slowly and cautiously.

Fig. 162. $^1/_1$–$^1/_3$

5. During the combustion there may be formed small amounts of oxides of nitrogen, and these passing to the potash bulb will be absorbed and count as carbon dioxide. The oxides are decomposed on contact with hot metallic copper, their oxygen combining with the metal. For this purpose a roll of copper foil is placed between the copper oxide and the asbestos plug next the cork at the front of the tube; the copper should be free from sulfur, and previously superficially oxidized and reduced to remove occluded hydrogen.

Behind the copper foil is another plug of asbestos, then a few inches of copper oxide whose purpose is to oxidize any volatile matter or carbon monoxide resulting from incomplete combustion. It is held to place by another asbestos plug. As substitutes for the copper oxide there have been proposed manganic oxide, or where the combustion is done in a stream of oxygen, platinized asbestos, or simply fibrous asbestos, the latter acting mechanically to promote the reaction between the carbon monoxide and oxygen.

Organic bodies containing sulfur are mixed with lead chromate, as this reagent both oxidizes sulfur and sulfurous acid and combines with sulfuric acid. Semi-organic bodies containing alkalies leave a residue of alkali carbonate on burning, and the results for carbon are consequently too low; such bodies are mixed with potassium bichromate and lead chromate, the excess of chromic acid in the former reagent expelling the carbon dioxide from the alkali carbonate.

Fig. 163.

6. The drying tube, Fig. 163, is provided with an extra empty bulb at A in order that the larger part of the water produced may condense therein, and the calcium chloride remain drier and more efficient from having less moisture to absorb. For the straight tube may be substituted a U-tube containing anhydrous phosphoric acid or glass splinters saturated with concentrated sulfuric acid, or a specially arranged tube holding both these absorbents which are more energetic desiccators than calcium chloride.

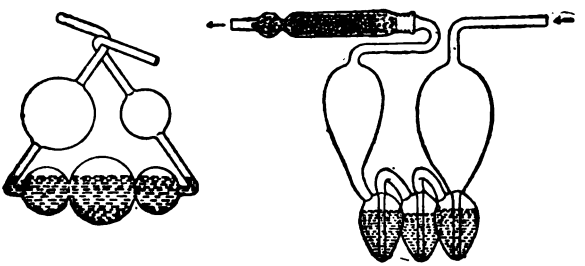

Fig. 164.

As an absorbent of carbon dioxide a strong solution of caustic potash or soda is the usual reagent. Numerous forms of containers have been invented, all designed to secure as intimate and prolonged contact be-

tween the lye and gas as possible, though the important feature of presenting a small surface of glass to the atmosphere has generally been neglected. The forms shown in Fig. 164 need no description; that of Bowen is one of the best in point of strength and compactness.

Since the current of unabsorbable gases passing through the bulb carries away a little moisture from the potash solution (unless it is unusually highly concentrated), a small calcium chloride tube is attached and weighed with it; in Fig. 164, the horizontal tube is fitted to the bulb by a ground joint.

In cases where a large weight of carbon dioxide is expected from a combustion two potash-bulbs should be joined tandem. Many believe that a U-tube filled with soda-lime (a mixture of granular sodium and calcium hydrates) is a safer absorbent for carbon dioxide than potash solution; the tube is guarded from loss of moisture by an attached tube of chloride of calcium. For the soda-lime tube some would substitute one filled with pumice fragments saturated with the strongest potash lye.

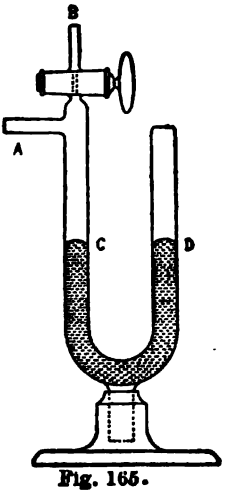

Fig. 165.

Before beginning a combustion the perfect gas-tightness of the corks and rubber connections must be assured. The tube A of a small mercury manometer Fig. 165, is connected to the exit tube of the potash bulb, and the entrance to the combustion tube is closed. Air is blown in at B until the mercury in C is depressed into the bend, and the stopcock is closed. If the inequality in height of the columns of mercury remains unchanged or nearly so for ten minutes, the connections may be considered tight, but it must be remembered that during this time any variation in the temperature of the air inclosed in the train will alter the pressure on the mercury. The usual directions are to produce a partial vacuum in the train instead of compression, but except where the tension during the combustion is to be less than atmospheric, the latter is the better plan, as an imperfect connection may yet be secure against external atmospheric pressure.

The details to be observed in making a combustion differ somewhat according to the character of the organic body and individual practice, but in any case require the undivided attention of the operator. The usual routine is about as follows, the directions applying to a porcelain or platinum tube and the use of a current of oxygen for oxidation.

The combustion tube having been cleaned and the copper oxide near the front placed in position, a current of pure dry air is passed through it to remove adhering moisture. A boat containing a known weight of some pure organic compound such as cane-sugar, is pushed to the middle of the tube followed by a roll of platinum gauze. The potash bulb and prolong and the chloride of calcium tube are weighed and connected to the combustion tube. Then the tightness of the connections is tested by the manometer.

The section of the combustion tube containing the copper oxide is heated to redness while a slow current of pure oxygen is passed through the apparatus. Then the burners beneath the platinum gauze are lighted, and finally those beneath the boat. The flames are raised until the tube is at a dull red heat. The sugar will be burned in a few minutes time, whereupon the stream of oxygen is replaced by one of pure air, and the flames gradually lowered and finally extinguished, those under the copper oxide last. When the air has displaced the (heavier) oxygen, the drying tube and potash bulb and prolong

are detached, their orifices closed by glass plugs or other means, allowed to cool in the balance case, and weighed.

The apparatus is now in readiness for the analysis of any organic substance, the combustion of sugar serving to indicate by the close agreement of the results with those calculated from the formula, that no defects exist in the apparatus or connections.

A roll of metallic copper in the combustion tube is unnecessary for non-nitrogenous bodies. In burning those containing nitrogen it is essential that the copper be not superficially oxidized, as it would then be powerless to decompose the oxides of nitrogen. For organic bodies containing a halogen, there may be interposed between the chloride of calcium tube and the potash bulb, a U-tube containing in one limb dry granular cuprous chloride to absorb halogen acids, and in the other limb silver foil to retain free halogens, and calcium chloride to absorb any water from the cuprous chloride.

For small amounts of organic bodies that are readily combustible, the current of oxygen may be dispensed with and air alone relied on for their oxidation. The process here is to be carried on more slowly than where oxygen gas is used. In either case, a blank combustion should not cause an increase in weight of the drying tube or potash bulb of more than a milligram.

Since the mixture of oxygen or air with a highly volatile liquid is explosive, the combustion of the latter is begun by passing a stream of pure, dry nitrogen until it is gasified, relying on the hot copper oxide to oxidize what vapor reaches it.

Levoir* proposes an apparatus for the combustion of organic compounds that dispenses with the ordinary combustion furnace. The compound is held in a small platinum tube and surrounds a spiral of platinum wire. The arrangement is placed in a glass combustion tube, the ends of the platinum wire projecting and the combustion tube filled with oxygen. An electric current is passed through the wire sufficient to heat it to redness, and the organic body burns rapidly in the oxygen.

Berthollet effects the combustion in a 'calorimetric bomb.'† This is a thick steel cup lined with platinum and having a tube projecting through the cover. A platinum basket containing the organic body is hung about the center of the cup and in contact with it is a thin platinum wire connected to platinum rods passing to the exterior of the apparatus. The cover is fastened on tightly and oxygen forced in until the pressure is about 25 atmospheres, the tube closed, and a current of electricity passed through the wire heating it to redness and igniting the organic body. The combustion is instantaneous and total. The resulting gases are withdrawn through the tube in the cover and passed through absorbing tubes as usual.

The ultimate analysis of a compound gas or a mixture of gases can be done by passing a measured volume through a combustion tube arranged as for volatile organic bodies. Or with the gas may be united a suitable proportion of oxygen, hydrogen, or oxyhydrogen, as needed, and the mixture exploded in a eudiometer or burned by platinized asbestos.

Moist combustion.‡ The elements of many organic bodies are oxidized partially or completely by the action of an aqueous solution of some strong oxidizer. Of the several reagents proposed, potassium permanganate and chromic

* Chem. News, 1890—1—87.

† *Idem*, 1888 - 2—284; Stillman Engineering Chem. 126.

‡ Analyst, 1898-99.

acid have a general application, while potassium manganate, chloric acid, hydrogen peroxide, lead peroxide, and others, are available only in special cases. According to the nature of the organic body and the oxidizer, acidity, temperature and time of digestion, and other conditions, there is determined: (1) the weight of oxygen required for oxidation, in which case the analysis is rather of the nature of a proximate than an ultimate one; or, (2) the weight of carbon dioxide produced, when the process is but a variation of the ordinary furnace combustion.

A. Oxidation by permanganate. Usually this reagent is applied in a solution made strongly alkaline, though sometimes in conjunction with sulfuric acid. The organic body, that may be soluble or insoluble in water, is digested with a measured excess of a standard aqueous solution of potassium permanganate under fixed conditions of time, temperature and concentration. In most cases the reaction ends with the removal of three atoms of the available oxygen from the reagent, leaving insoluble manganese dioxide, though under some circumstances all five atoms react. The temperature during the operation should be above 100° for complete oxidation (Wanklyn). Smith states that in an acid solution there occurs a secondary reaction between the precipitated manganic oxide and the excess of permanganate with liberation of oxygen, but that it may be prevented in great part by the presence of a sufficient quantity of ferric phosphate. If a chloride is contained in the organic body it will react with sulfuric acid to form hydrochloric acid, this decomposing permanganate.

After digestion for the specified time, the solution is either (1) filtered through asbestos and the excess of permanganate in the filtrate determined, either by direct titration by oxalic acid or ferrous sulfate, or better by a back titration by one of these and permanganate; or (2), the manganese in the precipitate is determined by a gravimetric or volumetric process; or (3), without filtration both the precipitate and excess of permanganate are reduced by excess of oxalic acid and the excess titrated back by permanganate. From the weight of oxygen consumed in the decomposition of the organic body sometimes a calculation may show the percentage of the oxidizable elements, but usually this is not to be relied on, for comparatively few bodies are completely oxidized by permanganate, and a partial oxidation is not so regular and definite that any positive conclusions can be drawn from the oxygen consumed — analogous bodies may react quite differently when treated under the same conditions.*

In the determination of carbon by oxidizing the organic body by permanganate and weighing the carbon dioxide produced, the evolved gas, as in a furnace combustion, is passed first over dry calcium chloride, then into potash solution. But for the permanganate it is better to substitute the (usually) more energetic oxidizer chromic acid in sulfuric acid solution.

For the determination of the humus of soils Warrington and Peake digest with permanganate first made alkaline by potassium hydrate, then after acidification by sulfuric acid. In the first digestion potassium carbonate and probably some potassium oxalate are formed; in the second the oxalic acid is decomposed by the permanganate, and the carbon dioxide formed, plus that liberated by the sulfuric acid from the potassium carbonate, is passed into a tube of soda-lime and the increase in weight found. Determinations by permanganate

* Journ. Anal. Chem. 3—387.

of carbon in a soil averaged 92 per cent of that given by tube-combustion, while the chromic acid process yielded only 80 per cent.

For the determination of humus in aqueous solution, Raulin * would apply the oxidizing power of recently precipitated manganic hydrate. He directs to prepare a liquid containing manganic hydrate in suspension by mixing solutions of potassium permanganate and manganous sulfate in the ratio of three molecules of the former to one of the latter, boiling until the mutual decomposition is complete. The solution of humus, in quantity not greater than will reduce one-half of the manganic hydrate, is added, and the mixture acidified by sulfuric acid and boiled for eight hours. The humus acts to reduce the manganic to manganous hydrate which then dissolves in the sulfuric acid. What manganic hydrate remains unacted on is determined by dissolving in standard oxalic acid, and titrating back the excess of the latter by permanganate. A blank determination is made with the same weights of reagents as were used in the analysis, and the difference in the volumes of standard permanganate is the basis for calculation.

B. Oxidation by chromic acid. Chromic acid in conjunction with sulfuric acid attacks a greater number of organic bodies than does permanganate. The reactions are $3C + 4CrO_3 + 6H_2SO_4 = 3CO_2 + 2Cr_2(SO_4)_3 + 6H_2O$; and $3H_2 + 2CrO_3 + 3H_2SO_4 = 6H_2O + Cr_2(SO_4)_3$. It is said that the celluloses and carbohydrates are entirely converted to gaseous products, as are some typical benzenoid compounds, and urea in presence of a little nitric acid, but the monobasic acids of the fatty series are not fully oxidized; amid and imid nitrogen prevent complete oxidation.†

Up to a certain concentration the aqueous solution of the two acids may be heated to boiling without an inter-reaction taking place; at a higher concentration the chromic acid is decomposed — $2CrO_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 3O + 3H_2O$ — the decomposition occurring at a lower temperature the greater the concentration. Hence the concentration of the reagent must be adjusted to the method employed, which may be (1), a determination of the oxygen consumed by the organic compound, where the secondary reaction would increase the result, and (2), a determination of the carbon dioxide evolved, where the event of the secondary reaction is immaterial.

(1). The determination of oxygen consumed has been applied by several chemists to various organic compounds. Heidenhain ‡ remarks that quantitative oxidation is possible only with a small number of substances, but almost quantitative results are obtained with very many substances. By experiment he found that 23 Cc. of fifth-normal potassium bichromate mixed with 15 Cc. of concentrated sulfuric acid could be boiled for 15 minutes without appreciable reduction of any chromic acid, and arranges that this concentration shall not be exceeded in the united volumes of the reagent and solution of the organic body. The mixture is heated to boiling for ten minutes in a flask provided with a simple form of reflux condenser to prevent evaporation of any great amount of water. The excess of chromic acid is determined by reduction by standard ferrous sulfate and back titration of the excess of the latter. The calculation is based on a factor derived from experiments on the chemically pure organic body; — usually but two determinations, namely of 100 per cent and 40 per cent, are needed to construct a table by interpolation.

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* Chem. News, 1890—1—155.

† *Idem*, 1888—2—21.

‡ Journ. Anal. Chem. 1893—71.

2. The more concentrated solution of chromic acid in stronger sulfuric acid has a broader application for the reason that most non-volatile organic bodies, either soluble in water or insoluble, are eventually completely oxidized. The advantages over the furnace-combustion process for the determination of carbon are the comparative simplicity of the apparatus, the possibility of analyzing moist or pasty matter without previous drying, and that fewer precautions are required for certain compounds, such as the organic salts of the alkalies. Against the process is the uncertainty of a complete oxidation of refractory bodies, necessitating an extra attachment for insuring the conversion of any carbon monoxide to dioxide, the long boiling needed for some compounds or forms of elementary carbon, the inapplicability to volatile bodies, and its limitation to the determination of carbon only.

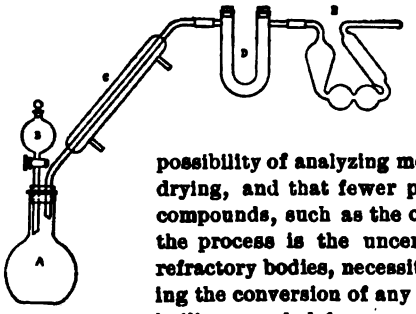

Fig. 166.

The usual train of apparatus is shown in Fig. 166. The weighed sample is dropped into the flask A and covered with a strong solution of chromic acid or potassium bichromate. The funnel-tube B is filled with concentrated sulfuric acid. Through a second hole in the cork passes the end of a reflux condenser C whose object is to condense the steam from A and return the water, in this way avoiding the rapid liquefaction of the chloride of calcium in the drying tube D. This tube is of a larger size than that of the usual combustion train since it is not to be weighed. The potash bulb E is one of the ordinary forms.

The apparatus is connected gas-tight, water started through the condenser, and the sulfuric acid run into A. When the evolution of gas slackens the solution is boiled and a current of pure air passed through the apparatus entering at the funnel tube. Finally the potash bulb is detached and weighed, observing the usual precautions.

During the boiling of the mixture in A some of the reagent may reach the cork or rubber stopper and act upon it with generation of carbon dioxide. To provide against this a flask can be had with a ground glass stopper in which is fused the funnel tube, the outlet tube projecting from the upper part of the neck of the flask.

Should the substance contain a halogen, the potash bulb is guarded by a tube containing a solution of silver sulfate. To insure the combustion of any carbon monoxide or hydrocarbons escaping from the flask, between the condenser and train there may be interposed a porcelain tube filled with copper oxide kept at a red heat. It should be remembered that any carbonate in the sample will also furnish carbon dioxide.

The process is largely used for the determination of the combined carbon of iron and steel, operating on the carbonaceous residue left after solution of the metal in certain reagents (*vide* Iron). To determine the carbon dioxide more rapidly than by absorption in potash and weighing, Phelps proposes to pass the gas into a known volume of baryta water, and titrate what baryta remains in solution. Handy* prevents absorption of carbonic acid from the air during the filtration by causing a current of purified air to play over the surface of the liquid in the funnel, then determines the baryta by standard acid.

Or the carbon dioxide may be passed into a gas-measuring tube, the volume observed and reduced to normal conditions, then into an absorption tube

* Journ. Amer. Chem. Socy. 1895—247.

containing potash lye, and the residual air, plus any oxygen evolved from the chromic acid, measured.

NITROGEN.

Nitrogen may be determined either (1), by the 'absolute method' of isolating it in the elementary form and measuring the gas; or (2), by converting it into ammonia, this to be determined gravimetrically, volumetrically, or by colorimetry.

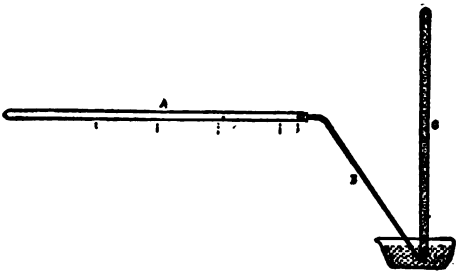

Fig. 167.

1. A. In the absolute method, originated by Dumas, the organic substance is burned by the oxygen from copper oxide, and the liberated nitrogen is separated from the water and carbon dioxide also produced, then measured in a gas tube and its weight calculated from its normal volume.

A hard glass tube A, Fig. 167, about 30 inches long, is closed at one end by fusion, and in it are charged in succession layers of potassium bicarbonate, copper oxide, a mixture of the organic body with copper oxide, a close roll of metallic copper, and alternate layers of copper oxide and metallic copper until nearly full. The front end is closed by a plug of asbestos behind a well-fitting cork. Through the cork projects a long glass tube, the outer part bent downwards and the end upwards to convey the gas into the measuring tube.

Preceding the combustion the closed end of the tube is heated until carbon dioxide from the bicarbonate has driven out all the air from the tube, this shown by passing a little of the escaping gas into a tube of potash lye, when all should be absorbed. Then there is placed over the end of B a graduated gas tube C filled with strong potash solution. The combustion tube is now heated, beginning at the front and proceeding until the bicarbonate is reached, which is again heated until the evolved carbon dioxide has swept all the gases into the gas tube. In the latter the steam condenses and the carbon dioxide and any traces of chlorine are absorbed, leaving only nitrogen. The tube is transferred to a jar of water, and the volume of moist nitrogen measured with the usual precautions, and reduced to normal conditions wherein one cubic centimeter of nitrogen weighs .00125616 gram. If through inadvertence a little nitrogen dioxide should have escaped decomposition by the copper and accompany the nitrogen, it may be absorbed by ferrous sulfate, and one-half ($N_2O_2 = N_2 + O_2$) the diminution in volume deducted.

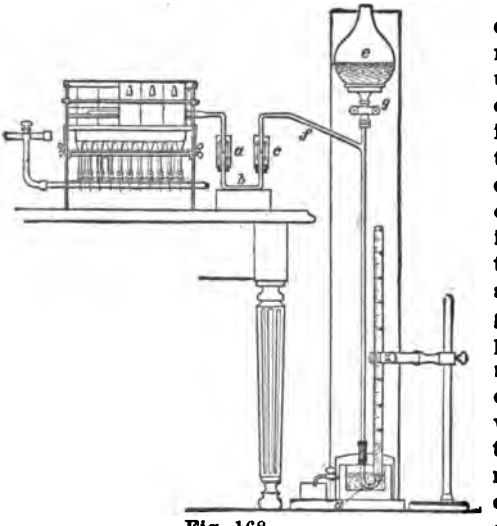

Fig. 168.

Of the many modifications of the details of the process there may be mentioned that of Simpson who substitutes a mixture of copper oxide and mercuric oxide for the copper oxide, and a mixture of magnesium carbonate and mercuric oxide for the sodium bicarbonate; of Johnson and Jenkins who aid the combustion by a little potassium chlorate in the extreme posterior of the tube, relying on the metallic copper at the anterior to fix any excess of oxygen generated from the chlorate; and of Meyer, who substitutes lead chromate for copper oxide to retain any sulfur gases coming from sulfur in the organic body.

Or the combustion may be conducted in vacuo, dispensing with the bicarbonate. The combustion tube, Fig. 168, is connected by rubber tubing to a Sprengel mercury vacuum-pump. To insure the air tightness of the connection it is surrounded at a and c by larger tubes containing glycerine or mercury. On opening the stopcock g a stream of mercury flows down the tube from the reservoir e, drawing air from the combustion tube until it becomes practically vacuous, the air escaping from d. A gas-measuring tube filled with mercury is then inverted over d, and the combustion tube (charged as above except the omission of the bicarbonate) is heated as before. The pump transfers the product of combustion to the gas tube. When the combustion is ended the gas tube is transferred to a trough of potash solution to absorb the carbon dioxide, and the volume of the residual nitrogen is read. A small error comes from the presence of occluded air or other gases in the tube, liberated on heating.

B. A number of organic bodies are decomposed by an alkaline solution of sodium hypobromite or hypochlorite, one of the products being gaseous nitrogen. The complete isolation of the nitrogen is seldom obtained however, though a nearly complete evolution may be had in some cases by the addition of a catalytic agent. The process has an extensive application for the determination of urea in urine, *q. v.*

2. A. In the method of Will and Varrentrapp the nitrogen of the organic body is converted into ammonia by heating with soda-lime; it is said that the conversion is effected through the dissociation of aqueous vapor — $3C + 2N + 3H_2O = 3CO + 2NH_3$. The ammonia is led through a mineral acid by which it is absorbed, and is determined by the usual methods for ammonia.*

The apparatus is shown in Fig. 169. The combustion tube, A B, that may be of glass or iron, contains at the sealed end a layer of oxalic acid or calcium oxalate which on heating decomposes with evolution of carbon monoxide and dioxide; next to this is the sample mixed with soda-lime or quick lime, and if rich in nitrogen, with some sugar or other non-nitrogenous substance whose gaseous products dilute the ammonia and lessen the danger of any passing the acid unabsorbed. The third layer is soda-lime only, held in place by a plug of asbestos. Joined to the combustion tube is a container for the acid, such as the "nitrogen bulb" C, partly filled with dilute hydrochloric acid. The combustion is carried on in the usual way, proceeding to heat the tube gradually back to the oxalic acid. When the gases from the decomposition of the latter have driven out the ammonia, the solution of ammonic chloride is poured into a beaker and precipitated by chloroplatinic acid with the usual precautions; the ammonium platinchloride may be

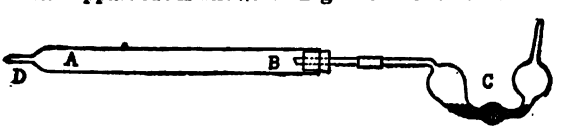

Fig. 169.

* Journ. Anal. Chem. 1888—335.

weighed as such, or the platinum separated by simple ignition or otherwise, and weighed.

It is more usual, however, to determine the ammonia in a volumetric way. Here the bulb contains a fixed volume of standard sulfuric acid, and after the combustion the unneutralized excess is titrated by standard alkali and litmus.

The method has the confidence of most technical chemists of affording accurate results when carefully worked; an especial precaution is that of limiting the heat to bare redness lest ammonia be dissociated. But some organic bodies yield volatile compounds when ignited with soda-lime, and cannot be analyzed by this method except with several modifications.

B. Ruffle's method* is similiar to the above, differing in that sodium thiosulfate, sulfur, and carbon or an organic compound are added to the soda-lime mixed with the organic body. These additions make it possible to convert the nitrogen of some compounds into ammonia, where soda-lime alone would fail. The reaction is said to be that the thiosulfate furnishes sulfurous acid which reacts with oxides of nitrogen to form ammonia and sulfuric acid, *e. g.*, $N_2O + 4SO_2 + 3H_2O = 2NH_3 + 4SO_3$.

Several other mixtures of a similar character to the above have been proposed. The Ruffle method is highly regarded by many chemists, especially for the determination of nitric nitrogen.

C. The method due to Kjeldahl, although of comparatively recent origin, has largely supplanted other methods. Its advantages are that it can be applied to heterogeneous mixtures difficult to powder, and to liquids, pastes and hygroscopic matter in general without previous drying; that the apparatus required is less complicated and more compact; and that a number of determinations can be carried on simultaneously by one operator.

A small weight of the organic body is heated with concentrated sulfuric acid until a clear solution results, when powdered potassium permanganate is sifted in. The liquid is diluted with water, made alkaline by sodium hydrate, and distilled until the freed ammonia has gone over with water. The receiver contains an acid to fix the ammonia, which is then determined as in the soda-lime process, *supra*.

The reactions occurring during the decomposition of the organic body have been described as follows: First, the sulfuric acid absorbs any water that the sample may contain; second, the acid reacts with the carbon and hydrogen to form carbon monoxide and water and is reduced to sulfurous acid; third, sulfurous acid and nitrogenous compounds dissociate water, the nitrogen takes up hydrogen forming certain intermediate products but ultimately ammonia, while the sulfurous acid is oxidized to sulfuric; fourth, the potassium permanganate completes the oxidation of any part of the substance resisting the sulfuric acid alone.

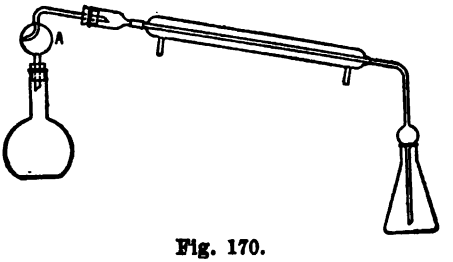

Fig. 170.

About one-half gram of the organic body is weighed; if a liquid it is placed in a bulb with a capillary neck. The substance is covered with ten to twenty Cc. of concentrated sulfuric acid, and the mixture boiled until all the organic matter has been destroyed and the acid become

* Chem. News, 1890—1—231; Journ. Chem. Socy. 40—451 and 21—161.

clear and colorless or but slightly tinted. The permanganate is added and the solution heated; then cooled, diluted with water, and transferred to a larger flask arranged for distillation as shown in Fig. 170. The condenser is of block-tin or platinum (since the ammonia would dissolve a little glass were the condenser of this material), or simply a long air-cooled tube, the exit dipping into the acid in the receiver,

Into the flask is poured an excess of sodium hydrate solution. The alkaline liquid is then distilled (best in a current of steam) until the ammonia has passed over into the acid. To prevent the carrying over of any of the alkaline liquid as spray, some form of trap is interposed between the flask and condenser; one is shown at A in Fig. 170.

The determination of the ammonium in the distillate can be done gravimetrically by conversion to ammonium platinchloride, but a volumetric method is more usual. Of the latter the plan of back titration by a standard alkali is most common; a variation is the use of baryta water with rosolic acid as indicator. Or the distillate may be treated with potassium iodide and iodate, when the free sulfuric acid liberates an equivalent of iodine — $5KI + KIO_3 + 3H_2SO_4 = 3K_2SO_4 + 3I_2 + 3H_2O$ — and the iodine titrated by thiosulfate and starch paste. A rapid approximate method is that of liberating nitrogen through the agency of sodium hydrate and hypobromite and measuring the gas. For small amounts of ammonia, Nessler's test is the most accurate.

Many modifications of the original method of decomposition by sulfuric acid have been proposed, but mostly of dubious worth.* Various oxidants or carriers of oxygen have been advised as additions to the sulfuric acid, such as cupric oxide, mercury, etc., the sulfates of these bases being supposed to materially assist in the dissolution of the organic body. An objection to the use of mercury, the most common addition, is the need of subsequent removal by a sulfide, and the inaccuracy following the introduction of an excess.†

Gunning modifies the method by the substitution of solid sodium pyrosulfate for sulfuric acid thus securing a more powerful oxidizing action. The process has received the favor of many chemists. Riviere and Bailhatche‡ prefer sodium pyrophosphite to the pyrosulfate.

As described, the original method is not suited for the determination of nitric nitrogen especially in presence of much chlorine. It is said that nitro, nitroso, azo, diazo, hydrazo, and amidoazo bodies and compounds of nitrous acids, the hydrazines, and probably cyanogen compounds cannot be satisfactorily determined. To adapt the method for nitrates, to the sulfuric acid Jodlbauer adds phenolsulfuric acid, zinc dust, and a few drops of platinic chloride solution; the nitric acid becomes nitro-phenol, this by the reducing action of zinc becomes amido-phenol, and this by the action of sulfuric acid becomes ammonia. Salicylic and benzoic acids are in use for the purpose, finally oxidizing the excess by permanganate, and it has been found of advantage to mix a nitrate with gypsum before the digestion.

THE HALOGENS.

In the method of Carius, the compound is oxidized by nitric acid in presence of silver nitrate, and the compound of halogen and silver weighed. A tube of stout glass is sealed up at one end, and the sample with some powdered silver nitrate introduced; if the organic body is a volatile liquid it is held in a weigh-

* Journ. Anal. Chem. 2—299.
† Journ. Socy. Dyers & Col. 1897—81.
‡ Analyst, 1896—267.

ing-tube closed by a glass stopper, or sealed up in a light glass bulb afterward broken by shaking the tube. Concentrated nitric acid is then poured in to partly fill the tube, and the open end is drawn out to a small bore and the orifice sealed by a blowpipe flame.

The tube is then heated in an oven for several hours at a temperature of from 150° to 300°, allowed to cool, held upright, and the tip of the prolong softened by a blowpipe flame, when the gases liberated by the reaction will force their way through the plastic glass; should inflammable gases have been formed, a safer plan is to cut off the end at once. The prolong is now broken off, the solution poured out, diluted, and the silver compound filtered and weighed. A simpler plan is to weigh the silver nitrate introduced with the sample, and determine what is left uncombined, easiest by titration with standard sodium chloride.

While the results of the method are unexceptionable, the length of time required for decomposition, the danger of explosion of the tube during the heating or on opening it, and various manipulative difficulties seriously detract from the usefulness of the method.

A solid substance may be calcined in contact with a base that will fix the halogens or their acids. Quicklime forms compounds of calcium that may be readily converted into corresponding silver compounds and weighed. Kopp's method is that of heating with ferric oxide in a tube open at one end, the reaction yielding soluble ferric haloids ready for precipitation by argentic nitrate. Kekule digests the substance with water and sodium amalgam whose action is to form the sodium salts; but the method is of limited application.

Meilliere evaporates a solution or extract with calcium nitrate in a platinum crucible, after which a slight ignition destroys all the organic matter. The aqueous extract of the residue is free from phosphates, and after acidulation with sulfuric acid and the addition of calcium carbonate to decolorize and neutralize the liquid, the halogens in the filtrate may be titrated by standard silver nitrate and potassium chromate.

Combustion in the calorimetric bomb of Berthollet may be applied to the determination of the halogens; for chlorine a little arsenious acid should be added to fix this element.

Plympton and Groves propose to burn the organic body in a Bunsen flame under an inverted funnel, drawing the products of combustion through the stem into a solution of sodium hydrate by which the halogens are retained.

SULFUR.

In the combustion of organic bodies containing sulfur there is formed sulfurous acid mainly, this converted to sulfuric by an oxidizer. In the furnace combustion for carbon and hydrogen the substance is mixed with lead chromate, or a mixture of lead chromate and potassium chromate, instead of copper oxide, since this compound both oxidizes the sulfurous acid and reacts with the sulfuric to form lead sulfate.

Sulfur is always determined by first converting it into sulfuric acid, then precipitating by barium chloride and weighing the precipitate of barium sulfate. Many schemes have been proposed for the oxidation.

One process is that of burning the organic body in a combustion tube in a current of mixed oxygen and nitric oxide.* The sulfur is thus brought to the highest state of oxidation and the acid may be caught in any convenient reagent. Prunier mixes the substance with 80 to 100 parts of powdered potassium per-

* Berichte, 19–1910; Chem. News, 1888–2–96.

manganate and heats the mixture in an ordinary combustion tube. Oxygen is given off from the permanganate at about 240°. The products of combustion are passed through a solution of potassium permanganate which absorbs the sulfuric acid and oxidizes any sulfurous acid. After filtering from deposited manganese oxide, the filtrate is acidified and the sulfuric acid precipitated as usual. Carbon may be determined in the same operation by annexing a tube of baryta water; after the combustion is finished the carbon dioxide is set free by a mineral acid and measured or absorbed and weighed.

The combustion may be made in oxygen under high pressure in a Berthollet calorimetric bomb containing a little water for the absorption of the sulfur oxides; a large percentage of sulfur is more readily oxidized if the organic substance has been mixed with an equal weight of a pure carbohydrate. Burton * modifies Sauer's method for liquids and gases by burning in a lamp or gas-burner, passing the gases formed in the combustion into a standard solution of potassium hydrate, and titrating back by a standard acid and methyl orange, this indicator indifferent to carbonic acid. Or the combustion gases may be passed through bromine water or a solution of bromine in hydrochloric acid for the oxidation of the sulfurous acid and retention of the sulfuric acid.

Oxidation in the wet way may be done according to the method of Carius for halogens, with the modification of omitting the silver nitrate. The solution after heating in the closed tube is evaporated to dryness, previously adding a little sodium nitrate; the residue is taken up by strong hydrochloric acid, diluted and filtered, and the sulfuric acid (now as sodium sulfate) precipitated by barium chloride, and the barium sulfate weighed as usual. For refractory bodies, such as asphalt, a preliminary digestion with fuming nitric acid is advised, and any residue left after heating in the tube is subjected to an examination for sulfur by one of the fusion methods mentioned below.

Some organic compounds are destroyed and the sulfur oxidized to sulfuric acid by heating with a liquid oxidizer. For this purpose there have been proposed nitric acid with potassium chlorate, potassium hydrate solution and the passage of a current of chlorine, alkaline potassium permanganate, chromic and nitric acids, etc. But many of these are likely to fail with bodies strongly resisting oxidation, however prolonged the digestion or boiling.

For decomposition in the dry way, Liebig's directions are to mix the substance with potassium nitrate or chlorate and project the mixture by small portions into potassium hydrate kept melted in a platinum crucible, finally heating over a blast-lamp. A later method is to melt the substance with a mixture of sodium carbonate and potassium hydrate and slowly add sodium peroxide until the carbon is burned.† It would appear that Eschka's scheme for sulfur in coals (*q. v.*) and cast iron could be extended to many other organic bodies.

Debus would mix the organic substance with potassium bichromate and sodium carbonate and fuse the mixture in a combustion tube; as a guard some of the reagent is placed before and behind the mixture. When the temperature has risen to redness a current of oxygen is passed into the tube until all the carbon has burned.

PHOSPHORUS.

Phosphorus is oxidized in much the same way as sulfur, Carius' method of decomposition and that of fusion with alkali carbonate and nitrate being most in use. After bringing the phosphorus to the state of phosphoric acid

* Amer. Journ. Science, 1889—472.
† Chem. Centralb. 1896—66.

the clear solution may be at once precipitated by magnesic solution, or in presence of metals forming permanent precipitates with ammonia, preceded by a separation as ammonium phosphomolybdate.

METALS.

The metals of semi-organic compounds may be converted into oxides or carbonates as the case may be, by ignition in air or oxygen until the carbon is burned. This is the simplest plan and is applicable for all metals that are not volatile at the heat of the calcination. For the volatile metals the organic matter may be oxidized by the method of Carius or by any of the liquid oxidizers mentioned under the determination of sulfur. After destroying the organic matter the determination follows the usual course of inorganic analysis.

COMBINATION METHODS.

Various schemes have been proposed for the simultaneous determination of two or more elements. That for carbon and hydrogen is entirely successful, but none of the others have come into general use, principally for the reason that the determination of any one element requires the careful adjustment of reagents and a certain peculiar routine of manipulation that must be more or less modified when another element has also to be determined.*

* Analyst, 1897—277; Amer. Journ. Sci. 41—40.

PROXIMATE ORGANIC ANALYSIS.

The processes for the separation and determination of organic bodies follow to some extent those for inorganic; but while to the latter we can apply, as a rule, a number of reactions that yield products suitable for weighing or measuring, the majority of organic compounds are indifferent to the common precipitants; again, for many inorganic compounds there are specific reagents allowing a perfect separation, while the number of specific reagents for organic bodies are comparatively few.

Another distinction is that with inorganic bodies the reagents have a broader scope, a given reagent being applicable in general to all or nearly all the combinations in which the reacting element or radical may enter, though for analytical purposes it may be restricted to a few or but one for practical reasons. But with organic compounds there enter into consideration the configuration of the molecule of which the group to be determined is a part, stereoisomerism, and the modification in behavior that substituted groups may undergo, these narrowing the scope of the various processes so far that there are but few that can be termed general for any one group.

A few characteristics not usually met with in inorganic bodies, such as volatility at moderate temperatures, solubility in organic liquids, an easily measurable boiling and congealing point, etc., are applied analytically.

In the practice of proximate organic analysis we may be called on to investigate —

1. A single organic compound, presumably pure, which is to be identified or classified, elementary analysis failing to disclose the constitution further than can be deduced from an empirical formula. Here a determination of some one group of the molecule — hydroxyl, ethoxyl, diazo, etc. — will be a basis for the calculation of the rational formula and structural constitution.

2. A similar case is where the compound is semi-organic. Usually the determination of the inorganic part and an elementary analysis of the organic part can be done by simple and accurate processes and often suffice to describe the compound; if not they are supplemented by a determination of one or more of the radicals.

3. A mixture of several organic compounds. The constituents may be either analogous bodies, as mixtures of different oils, waxes, vegetable alkaloids, artificial dye-stuffs, fruit essences, etc., or heterogeneous, as are many natural and manufactured articles. In the analysis of the former class, attempts at a separation of the constituents by methods designed for the determination of one of them, will often fail on account of the similarity of behavior of the others toward the reagent. Fractional solution, fractional precipitation, fractional distillation, etc., may be made to yield a fair separation, but as a rule, attributive methods are the main resource. Heterogeneous mixtures present fewer difficulties, and often admit of quite accurate separations.

4. Lastly, we may have to consider heterogeneous natural or artificial products that are partly inorganic. Such are animal and vegetable matter generally, animal secretions and excretions, medicinal preparations, the waste products

of manufactures, etc., etc. With material so diverse, no general statement can be laid down as to the methods available, since each example is a special problem and often one of no inconsiderable difficulty.

We may here glance at the methods commonly used.

SOLUTION.

Of organic bodies in general, water or one of the common organic liquids will serve as a solvent for the majority; the employment of the mineral acids, so frequent in inorganic analysis, is here comparatively rare. Lyes of the caustic and carbonated alkalies will dissolve a few bodies that are insoluble in other menstrua, and a few are only dissolved by concentrated sulfuric acid. Special solvents have a considerable use for separations.

DETERMINATION.

1. By evaporating the aqueous or other solution of the compound and weighing the residue. This, the simplest plan, is not practicable in many cases; volatility of the organic body, increased by the vaporization of the solvent, may cause a serious loss; a reaction between the solvent and solute may be set up at temperatures above ordinary; and the heat applied to evaporate the solvent may cause partial decomposition, and contact with the air allow oxidation, especially about the period of solidification.

The usual plan is to pour the solution into a tared flat-bottomed dish and evaporate at as low a temperature as practicable, finally drying the residue at a gentle heat or in the desiccator. Spontaneous evaporation is safer for slightly volatile bodies, and evaporation in vacuo is often a necessary precaution.

2. By precipitation of the organic body. The solvent may be changed to one in which the compound is much less soluble, *e. g.*, by the large dilution of an alcoholic solution with water. The result of the determination is generally too low from the incomplete insolubility of the compound in the mixed liquids. The accuracy is increased by removing by evaporation at a low heat as much of the original solvent as can be done without separation of the compound; though if the application of heat is allowable, the process of (1) is to be preferred.

Another plan for reducing the solvent power of the liquid is that of saturating the solvent with some inorganic salt—'salting out.' Aqueous solutions of some dyes, proteids, etc., are precipitated nearly completely by stirring in solid sodium chloride, magnesium sulfate, or similar salt, until the liquid is saturated therewith.

A few bodies in aqueous solution coagulate when the liquid is boiled or upon the addition of an acid, alcohol, or a ferment.

Rarely do organic compounds unite as a whole with a reagent to form an insoluble precipitate. An instance is the combination of aniline with chloroplatinic acid — $2C_6H_5NH_2 + H_2PtCl_6 = (C_6H_5NH_2HCl)_2PtCl_4$.

3. By volumetric analysis. Some organic bodies admit of direct titration by the common volumetric solutions or those of special reagents. It must be remembered that the ionic combination in which a group exists in the solution of an organic compound determines whether the reaction on which a titration is based will or will not take place.

Free bases, such as phenylhydrazin, antipyrine, etc., are titratable directly by a standard acid and suitable indicator, and this is also possible of a combination of a strong base with an acid weaker than the indicator selected.

Similarly, the free organic acids are titrated by standard alkali. If, for lack

of a suitable indicator, or on account of a highly colored titrate, a direct titration is difficult, the acid is treated with an excess of standard sodium hydrate, an excess of ammonium chloride added, and the ammonia set free by the excess of sodium hydrate is distilled into water and titrated by an acid. Or sodium carbonate may be mixed with the acid solution and the freed carbon dioxide dried and passed into potash bulbs and weighed. Compounds of a weak base and a strong acid, *e. g.*, the sulfates of the aromatic amines, some alkaloidal chlorides, etc., can be titrated by alkali as though the acid radical were combined with hydrogen.

Of occasional use are strong reducing solutions for oxidizable compounds, such as stannous chloride for reducing nitro-groups to amino-derivatives, and oxidizing solutions for reducible compounds. Arsenic acid oxidizes phenylhydrazin to phenol; beta-napthol in a carbon tetrachloride solution is converted to monobromnapthol by titration with bromine; hydrazin is converted by potassium permanganate to nitrogen, water and ammonium sulfate; hydroxylamin to nitrogen and water by vanadic acid, etc.

4. By determination of some element or radical of the organic compound, and calculation to the original body. When nitrogen, sulfur, or phosphorus is a constituent, the determination of the element is comparatively easy and accurate; however, the percentage of the element in the compound is usually quite small, and in the calculation of the latter from the former the errors of determination are correspondingly magnified.

Nitrogen is determined by the methods of ultimate organic analysis. A number of organic bodies are usually calculated from the nitrogen contained in preference to direct weighing, notably the proteids, the multiplier in this case being 6.25 or 6.33, since the average nitrogen content of proteids is about 16 per cent. Another example is the analysis of commercial Prussian blue (principally ferric ferrocyanide $3Fe(CN)_2.4Fe(CN)_3$); multiplication of the found nitrogen by the factor 4.4 gives approximately the weight of true pigment in the sample, the other constituents being nitrogen-free.

A large number of nitrogenous organic bodies are decomposed by certain well-known reagents, the nitrogen being evolved quantitatively or nearly so. Thus, diazo-compounds by boiling with dilute sulfuric acid, phenylhydrazin with iodine, hydrazides with Fehling's solution, and hydrazine salts with platinic chloride or potassium permanganate. Some reagents containing nitrogen are themselves decomposed and the total nitrogen obtained in the determination is the sum of that coming from the organic compound and the reagent; thus aspartic acid with nitrous acid yields malic acid and nitrogen — $C_4H_7NO_4 + HNO_2 = C_4H_6O_5 + N_2 + H_2O$; similarly, the aliphatic amines.

For a determination, the organic body is treated in a small flask with the reagent, and the evolved nitrogen conducted into a gas-measuring tube. The weight of nitrogen is calculated from the corrected volume. Another form of apparatus that may be used is that shown in Fig. 120.

Certain nitrogenous compounds, such as the nitrophenols, on heating with zinc-dust and mercury are converted first to amidophenols, then to ammonium sulfate. The ammonia in the product is determined.

From a few bodies, as the thioureas, sulfur is precipitated directly by ammoniacal silver nitrate and the silver sulfide formed converted to metallic silver by ignition. Other bodies are decomposed with the formation of an insoluble metallic sulfide when an aqueous solution is digested with a metallic oxide. But in general, sulfur is determined by oxidation to sulfuric acid, as by the plan of Carius, by fusion with an alkali carbonate and nitrate or other

oxidizing mixture, or by suspension in potash lye through which chlorine is passed. The sulfuric acid is determined in the usual way.

Phosphorus is a normal constituent of some animal and some vegetable matters. It is oxidized to phosphoric acid by proceeding as for sulfur, and the phosphoric acid determined as the magnesium compound.

5. By the weight of a reagent required to change the molecular structure. Many of these reactions have been applied in technical analysis, and for uniformity and comparison, a certain fixed weight of the material is taken for each test, and the result of the determination called the 'value' or 'number' of the material. For example the 'saponification value' of a wax is the number of milligrams of potassium hydroxide combining with the acids from one gram of the wax; the 'iodine number' is the weight of iodine entering 100 grams of an organic compound; similarly the 'acetyl number', 'carbonyl number', 'methoxyl number', etc.

A. By precipitation. With some classes of organic bodies certain inorganic and organic reagents produce compounds more or less insoluble. In a few instances the insolubility is sufficient to allow an accurate determination, but the majority are too freely soluble to admit of more than approximate results. Instead of directly weighing the precipitates, it is often better to determine some element or radical contained. Some of the principal reactions follow.

Phenylhydrazin (a colorless oily compound $C_6H_5N_2H_3$), phenylhydrazin hydrochloride, and various substitution products, all yield phenylhydrazons with bodies containing the carbonyl group. The products separate in the form of crystalline, flocculent, or oily compounds, most readily and completely from warm acetic acid solutions. The reaction has received considerable practical application in the determination and differentiation of the sugars. The precipitates may be dried and weighed; or, since phenylhydrazons are not decomposed by Fehlings solution, a known weight of phenylhydrazin hydrochloride is used for the precipitation and the excess determined by boiling with Fehlings solution; the nitrogen of the reagent is liberated, and is measured after passing into a eudiometer.

Carbamyl chloride reacts with hydroxyl derivatives with the formation of carbamates and hydrochloric acid. The reaction takes place at ordinary temperatures in ethereal solution. In the crystalline precipitate is determined nitrogen, this equaling the number of hydroxyl groups in the original.

Phenyl isocyanate gives ethereal phenyl-carbamates with hydroxyl compounds — $R.OH + C_6H_5N.CO = R.C_6H_5.NH.CO.O$. The reaction takes place at a boiling temperature. The product is washed by ether and cold water, and recrystallized from alcohol.

Sodium sulfite throws down crystalline precipitates from concentrated solutions of the aldehyds; for example, $CH_3.COH + NaHSO_3 = CH_3.CHOH.NaSO_3$ (sodium-oxyethyl sulfonate).

Iodine forms additive or substitutive compounds with many organic bodies, *e. g.*, with diazo compounds — $CHN_2.COO.R + I_2 = CHI_2.COO.R + N_2$. For pure organic bodies a simple plan of determination is to incorporate an excess of iodine with the alcoholic solution of the body, evaporate to dryness, expel the excess of iodine by a gentle heat, and weigh the residue; bodies insoluble in alcohol can be triturated with iodine and the excess volatilized. The method pursued for glycerides is described under Oils. A reaction of practical importance is that between aceton and iodine, iodoform being produced — $C_3H_6O + 2I_2 + KOH = CHI_3 + CH_3COH + KI + H_2O$.

Iodoso compounds react with hydriodic acid, being reduced to iodides and

liberating iodine from the reagent; thus, C_6H_5IO (iodosobenzene) + $2HI$ = $C_6H_5I + I_2 + H_2O$.

B. By the introduction of a determinable element or group. An organic radical is introduced into the molecule of the organic compound and afterwards determined; for example, the replacement of the hydrogen of a hydroxyl group of a compound by an acetic, benzoic, or phenylsulfuric group.

Replacement by the acetyl group is a common analytical scheme for the determination of organic acids, certain oils, phenols, amines, alcohols, etc. The acetylation is done by different reagents according to the character of the molecule to be acted upon; namely by treating the compound, or its solution in an organic solvent, with acetic anhydride, acetyl chloride, or anhydrous acetic acid and phosphorus oxychloride, then heating to a specified temperature under atmospheric or a higher pressure. For example —

$(OR)_2.C_3H_5.OH$ (a diglyceride) + $(C_2H_3O)_2O$ (acetic anhydride) = $(OR)_2.C_3H_5.O.C_2H_3O + C_2H_3O.OH$ (acetic acid).

$C_5H_{11}.OH$ (amyl alcohol) + $CH_3.COCl$ (acetyl chloride) + K_2CO_3 = $C_5H_{11}O.CO.CH_3$ (amyl acetate) + $KCl + KHCO_3$.

$3(C_6H_5)OH$ (phenol) + $3CH_3COOH$ (acetic acid) + $POCl_3$ (phosphorus oxychloride) = $3(C_6H_5)(C_2H_3O_2)$ (phenyl acetate) + $3HCl + H_3PO_4$.

The determination of the introduced acetyl group can be done in some cases by noting the increase in weight of the compound due to the assimilation of C_2H_2O (that is, C_2H_3O minus H). Another plan is to weigh the acetic anhydride taken for the acetylation, and after the reaction is complete, to convert the excess into acetic acid by treatment with hot water — $(CH_3)_2C_2O_3 + H_2O$ = $2CH_3COOH$ — and determine the acetic acid by titration with standard alkali, calculating the result to acetic anhydride. The weight reacting with the organic body is found by difference.

The most common method is that of separating the acetylated compound from the excess of the reagent, then hydrolyzing it by the action of water, an acid, or a solution of a caustic alkali or earth, and determining the acetic acid produced from the acetyl radical. Thus, the product in the first equation, *supra* —

$(OR)_2.C_3H_5\ OC_2H_3O + H_2O = (OR)_2.C_3H_5.OH + CH_3.COOH$ (acetic acid). The freed acetic acid is titrated by standard alkali. Another plan is to hydrolize the derivative by potassium hydrate solution, acidify by phosphoric acid, and distill the free acetic acid. In the distillate the acid is neutralized by baryta, the excess of baryta removed by passing carbon dioxide, and the baryta, in solution as barium acetate, determined gravimetrically and the acetic acid calculated.

Along similar lines the methyl group may be introduced into a compound by the agency of methyl iodide, the propionic radical by propionic anhydride, etc.

Benzoyl chloride and its various derivatives are employed to introduce the benzoyl radical into bodies containing the hydroxyl, amino or imide groups, reacting, in presence of sodium hydrate, with alcohols, phenols, amines, and amido-phenols to form crystalline precipitates, *e. g.*

$C_6H_5.OH$ (phenol) + $C_6H_5.CO.Cl$ (benzoyl chloride) + $NaOH = C_6H_5\ O.CO.C_6H_5$ (benzoicphenyl ester) + $NaCl + H_2O$.

$C_6H_5.NH_2$ (aniline) + $C_6H_5.CO.Cl + NaOH = C_6H_5.NH.CO.C_6H_5$ (benzanilid) + $NaCl + H_2O$.

The benzoylation is usually carried on in dilute aqueous solution made strongly alkaline, and at ordinary temperatures. The benzoyl derivatives are

usually white crystalline precipitates that retain traces of the reagent with some tenacity. The determination of the benzoyl radical is done by hydrolizing the derivative, it becoming benzoic acid. The hydrolysis is effected by hydrochloric acid saturated with benzoic acid, heating the mixture in a closed flask. The benzoic acid remains as a powder (solubility in water 1 in 400), and is filtered and washed with water saturated with benzoic acid. The filter and contents are thrown into water and the acid titrated by standard alkali and phenolphthalein. Or the benzoyl derivative may be hydrolyzed by alcoholic sodium hydrate, the liquid acidified by phosphoric acid, and the benzoic acid distilled over in a current of steam; the acid in the distillate is titrated as before.

Compounds containing the carboxyl group are etherified on boiling with absolute alcohol containing gaseous hydrochloric acid. The resulting esters are then determined by saponification with alkali in the usual way.

Aldehyds and ketons react with hydroxylamin to form oxims, respectively aldoxims and ketoxims; for example —

$C_6H_5.COH$ (benzoic aldehyd) $+ NH_2OH$ (hydroxylamin) $= C_6H_5.CHN.OH$ (benzaldoxim) $+ H_2O$.

$C_6H_5.CO.C_6H_5$ (diphenyl keton) $+ NH_2OH = C_6H_5.CNOH.C_6H_5$ (benzophenon oxim) $+ H_2O$.

The oxim is produced by acting on the organic body by hydroxylamin hydrochloride and sodium carbonate. The oxims as a class are crystalline compounds soluble in water from whence they may be extracted by agitation with ether.

C. A reaction yielding a determinable extrinsic product. The free carboxyl group is usually determined by titration of the compound by standard alkali, but if circumstances render this proceeding difficult, an indirect process may be substituted. One of these is based on the liberation of an equivalent of hydrogen sulfide from a soluble sulfide by a free organic acid — thus, $CH_3.COOH$ (acetic acid) $+ NaHS$ (sodium hydrosulfide) $= CH_3.COONa$ (sodium acetate) $+ H_2S$. The volume of the gas evolved is determined by conducting the operation in a modified form of the familiar Victor Meyer vapor density apparatus. Or the acid is dissolved in alcoholic potash in excess, the liquid compounded with strong alcohol, and carbon dioxide passed through it to convert the excess of potassium hydrate into carbonate and bicarbonate which precipitate. After filtering, the potassium in the solution (combined with the organic acid radical) is determined by the usual method.

Organic acids liberate iodine from a mixture of potassium iodide and iodate; *e.g.*, $6R.COOH + 5KI + KIO_3 = 6R.COOK + 3I_2 + 3H_2O$. The iodine is determined by treating the liquid with potassium hydrate and an excess of hydrogen peroxide, when a molecule of oxygen is liberated for every molecule of iodine — $I_2 + 2KOH + H_2O_2 = O_2 + 2KI + 2H_2O$. The volume of oxygen is found by having the reaction take place in a nitrometer or similar instrument.

The iodoso (IO) and the iodoxy (IO_2) groups liberate iodine from an acid solution of potassium iodide, the former freeing two atoms, and the latter four atoms, corresponding to their oxygen content.

The amids and amido-compounds are decomposed by contact with nitrous acid evolving nitrogen —

$C_2H_3O.NH_2$ (acetamid) $+ HNO_2 = C_2H_3O.OH$ (acetic acid) $+ N_2 + H_2O$.

one-half of the total nitrogen coming from the amid.

Zeisel's method * for the determination of methoxyl is one very generally

* Chem. News, 1891—1—37 and Analyst, 1898—297.

applicable. The principle is the conversion of the methyl group into methyl iodide by acting on the organic body with hydriodic acid — $R.CH_3O + HI = CH_3I + R.OH$ — then converting the methyl iodide into silver iodide by means of an alcoholic solution of silver nitrate — $CH_3I + AgNO_3 = AgI + CH_3NO_3$.

The apparatus for the determination is in three parts joined by rubber tubing; (1), a flask closed by a cork carrying a tube through which carbon dioxide enters and passes through the entire apparatus, and a reversed condenser to return water-vapor to the flask; (2), a guard-tube, arranged to be heated to about 56°, holding water in which red phosphorus is suspended, or a solution of potassium arsenite; and (3), a train of absorption bulbs containing an alcoholic solution of silver nitrate.

The apparatus is connected air-tight, the organic body and an excess of hydriodic acid placed in the flask, and all the air in the train displaced by carbon dioxide. The mixture in the flask is boiled, and the gaseous iodmethyl passes over, through the guard tube in which any hydriodic acid or iodine that might accompany it is retained, into the absorption bulbs where silver iodide is precipitated. The precipitate is purified and weighed. Volatile organic compounds may be analyzed if precautions are taken against their distillation. The method cannot be used where sulfur is a constituent of the organic body.

The withdrawal of the methyl group from a compound is known as demethylation, and has some applications in analysis. Thus, guaiacol is reduced to pyrocatechin and homopyrocatechin by the action of hydrobromic acid — $C_6H_4.OH.O.CH_3 + HBr = C_6H_4(OH)_2 + CH_3Br$. — these products extracted by ether, and subsequently separated by benzene.

Easily reducible metallic salts are acted on by some organic bodies with separation of the metal or a lower oxide. Silver nitrate is reduced to metallic silver by many organic compounds, in some instances in molecular ratio. The reduction of a cupric salt to cuprous oxide is familiar through the many applications of Fehlings solution to organic analysis. Other reagents that have a more limited use are mercuric, stannic, and arsenic compounds.

The reduction of potassium permanganate and potassium bichromate have been utilized for determinations of sugars, organic acids and their salts, and the like, as has the reduction of ferric chloride to ferrous chloride by hydrazin, hydroxylamin, and similar bodies.

6. Colorimetrically. Many organic bodies are intrinsically or after alteration by the action of reagents, of a color sufficiently pronounced for a colorimetric comparison.

Various compounds, notably the vegetable alkaloids, develop intense colors with certain reagents, but the colors are evanescent and greatly modified by associated bodies.

The pentosans and pentoses produce with phlorglucin and hydrochloric acid a cherry-red color that allows a fair comparison. The aldehyds reproduce the red color of fuchsin solution that has been previously decolorized by sulfurous acid.

7. Attributive methods. In inorganic analysis one elects attributive methods in preference to direct determinations for considerations of rapidity or convenience, but in organic analysis their employment is frequently a matter of necessity from the want of other methods.

Inequality in specific gravity is often applied in technical work to mixed liquids or solutions and occasionally to solid mixtures. Tables are drawn up from direct experiments showing the gravity corresponding to each percentage of

one constituent of the mixture, usually, however, extending only through the range of the proportions commonly found in commercial articles. Of the other physical data, the rotation of polarized light is largely applied in the determination of sugar, less often to the oils, urine, the proteids, etc.

The conducting power of solutions for electricity has been employed for the determination of the basicity of organic radicals combined with sodium. The salt is made up in a dilute aqueous solution, usually one gram-molecule in 32 and 32^2 liters, and an electric current passed through it by electrodes of platinum covered with platinum black. The resistance of the solution is measured by a modified Wheatstone's bridge, the adjustment indicated by a telephone and commutator in the circuit.

Of the chemical methods, the reacting quantity to a given reagent is often great enough between members of a mixture to be a reliable basis for a calculation.

The saponification value is of service in the analysis of mixtures of oils, waxes, etc., but even though the values of the members may differ considerably, in many instances they are too uncertain to be relied on, varying to an excessive degree by reason of origin, age, mode of preparation and other factors; *e. g.*, the saponification value of oil of rose geranium may be anywhere from 32 to 75 according to the locality of the growth of the plant.

The combining equivalent of the members of a chemical series will often show a scale of numbers increasing or decreasing regularly with the rank of the members. Thus, the formic acid series, each acid combining with a specific proportion of barium to form a neutral salt, ranging from 28.60 per cent for capric acid to 70.25 per cent for formic. In a mixture of any two of the acids the weight of barium needed for neutralization is d in the usual formula.

In the ash of commercially pure organic substances the ratio of one base to another is practically constant and may be used as a basis for the determination of an impurity or associate.

The ratio between the oxygen consumed from potassium permanganate and potassium bichromate in the moist oxidation process is said to be specific for some organic bodies — thus starch and sugar withdraw much more oxygen from bichromate, while the reverse is true of tannin.*

SEPARATION.

By solvents. The following scheme † aims to separate mixtures of the common organic bodies into four groups by the application of various solvents in succession. It is understood that in most cases the separation is but approximate.

On agitating the solid or liquid mixture with water acidulated by sulfuric acid and a suitable solvent immiscible therewith (ether, chloroform, amyl alcohol, benzene, or petroleum ether), the following distribution will occur:

A.

The Acidulated Aqueous Liquid will contain *carbohydrates, soluble alkaloids* and *acids, organic bases, proteids*, etc., which may be further separated by adding a moderate excess of soda, and again shaking with a suitable immiscible solvent, when there will be obtained: —

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* Journ. Amer. Chem. Socy. 1898—496.

† Allen, Coml. Org. Anal. 1—60.

IN THE ALKALINE AQUEOUS LIQUID —

Carbohydrates; as sugars, gums, dextrin.

Soluble Alcohols; as methyl alcohol, ethyl alcohol, glycerine.

Soluble Acids; as acetic, oxalic, lactic, malic, tartaric, sulphophenic.

Certain Alkaloids or *Organic Bases;* as curanine, urea, glycocine, solanine, and possibly cinchonine, morphine and pyridine.

Certain coloring matters; as indigo products.

Proteids and their allies; as albumin, casein, gelatin.

IN THE IMMISCIBLE LAYER —

Most *Vegetable Alkaloids;* as quinine, strychnine, aconitine, atropine, nicotine cinchonine, morphine, (the last two with difficulty).

Coal Tar Bases; as analine and its homologues (rosaniline), chrysotoluidine (pyridine), homologues of pyridine.

B.

The Immiscible Layer will contain *hydrocarbons, oils, various acids, resins, coloring matters, phenols, glucosides,* etc., which may be further separated by agitating the liquid with water containing caustic soda, when there will be obtained:

IN THE ALKALINE AQUEOUS LIQUID —

Fatty Acids; as stearic, oleic, valeric.

Various other Acids; as benzoic, salicylic, phthalic, meconic.

Acid Dyes and Coloring Matters; as picric and chrysophanic acids, alizarin, aurin, bilirubin.

Acid Resins; as colophony.

Phenols; as carbolic and cresylic acids, thymol, creasote.

Certain Glucosides, etc.; as santonin, cantharidin, picrotoxin.

IN THE IMMISCIBLE LAYER —

Solid Hydrocarbons; as paraffin, naphthalene, anthracene.

Liquid Hydrocarbons; as petroleum products, rosin-oil, benzene.

Essential Oils; as turpentine.

Nitro-compounds; as nitro-benzene.

Ethers and their Allies; as ether, chloroform, compound ethers, nitro-glycerin.

Fixed Oils, Fats, and Waxes.

Neutral Resins and Colouring Matters.

Camphors; as laurel-camphor, borneol, menthol.

Alcohols insoluble or nearly insoluble in water; as amyl and cetyl alcohols, chloresterin.

Certain Glucosides, etc.; as saponin, digitalin, santonin.

Certain Weak Alkaloids; as caffeine, colchicine, narcotine, piperine, theobromine.

After this partial separation, the four liquids are further treated, either in the same manner with other solvents, or otherwise, as the nature of the substance seems to call for.

Separation by precipitation, crystallization, distillation. As in inorganic analysis, in some instances the members of a group of allied bodies can be separated by successive precipitations. Thus, a separation of the proteids by the method of Schjerning * —

A. Albumin I is precipitated by tin chloride.

B. Albumin I, albumin II, and denuclein by lead acetate or mercuric chloride.

C. Albumin I, albumin II, denuclein and propeptone by ferric acetate.

D. Albumin I, albumin II, denuclein, propeptone and peptone by uranium acetate.

E. Albumin I, albumin II and propeptone by magnesium sulfate. The weights of the several precipitates are sufficient data for calculating the proportion of each proteid.

Fractional precipitation is applied to certain groups all of whose members

* Zeits. anal. 1898—413.

form precipitates of varying solubility with a given reagent; *e. g.*, the toluidins with oxalic acid, the acid oxalate of paratoluidin requiring 6600 parts of water for solution, and the corresponding ortho compound only 200 parts.

Distillation as a means of separating a volatile from a non-volatile body has many applications in technical analysis, as has fractional distillation for the approximate separation of complex liquids all of whose members are volatile at a moderate heat, *e. g.*, petroleum, liquid fatty acids, the isomers of the oxycarbonic acids, etc. As circumstances dictate, the distillation is conducted in a current of some gas or steam, or in vacuo.

Duclaux has described a method for the determination of the proportions of the volatile members of the fatty acid series in a mixture of two or more — namely formic to caproic. On distilling a dilute aqueous solution of any one of these acids the acid comes over with the water at a specific rate. Shown graphically in Fig. 171 are the results obtained by him for the first six acids of the series. The experiments were made by fractionally distilling 110 Cc. until 100 Cc. had come over, receiving each ten Cc. separately and determining the amount of acid it contained. The ordinates represent the percentages of acid in the distillate and the abscissae the percentages of the volumes of the distillate, taking the acid in the original 110 Cc. as 100 per cent. It will be seen that of formic and acetic acids the acidity of the vapor is less than that of the liquid throughout the distillation, though increasing in strength as the operation proceeds, while the reverse is true of the other four acids; and that in the residue of ten Cc. in the retort there were retained of formic acid 36.5 per cent, of acetic 20 per cent, etc., but none of caproic.

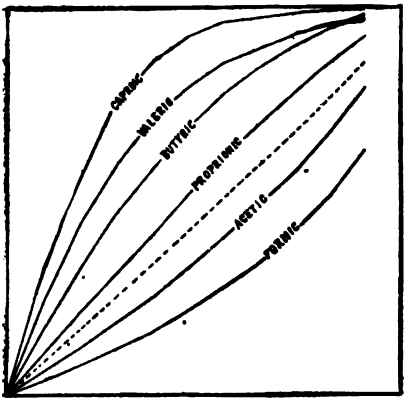

Fig. 171.

With a mixture of two acids the curve of the rate of distillation lies between those of the constituents, approaching the one whose proportion in the mixture is the greater. The dotted line represents a mixture in equivalent proportions of acetic and propionic acids.

In practice the total acidity of a mixture of the free acids is determined volumetrically by neutralizing them by a standard alkali; they are again set free by an excess of (non-volatile) sulfuric acid and fractionally distilled. But practically, the curves are so altered by the effect of condensation in the retort (page 225) that the method is restricted to the identification of one or possibly two acids in a solution.

Separation by ferments. Of the ferments that convert organic matter into less complex products, the most familiar is brewers yeast, well known for its action on the starches and sugars. Diastase and taka-diastase are convenient and powerful agents for the saccharification of starch, and inulase for the conversion of inulin to levulose. Brewers yeast allows the aldoses to be differentiated, only the tri- hex- and nonoses fermenting, and it is said that in a solution of ammonium paramandalate the micro-organism *pennicillium glaucum* destroys only the laevo-modification, while *sacchr. ellipsodeus* destroys only the dextro-modification.

An oxydase known as laccase obtained from the sap of the lac-tree of Japan,

is a soluble oxidizing ferment; added to a phenol, the mixture absorbs oxygen from the air — thus, in four hours, with hydroquinon there was absorbed 32 Cc. of oxygen per gram of hydroquinon; with pyrocatechin, 17.4 Cc. per gram; and with resorcin, only .5 Cc.*

Saponification — the conversion of an acid-ester into an acid and an alcohol — is of importance in many branches of technical analysis, notably as a means of parting certain oils, waxes, etc. from non-saponifiable matter in general. The reagent most used for the purpose is a caustic alkali in alcoholic or concentrated aqueous solution.

Other bodies that may be termed saponifiable in a broader use of the term are the amids — *e. g.*, $C_2H_3O.NH.C_2H_5$ (ethyl acetamid) + $NaOH = NH.C_2H_5.H$ (ethylamin) + $NaC_2H_3O_2$ (sodium acetate); amido and nitrile groups, hydrolyzed to ammonia; the higher alcohols of the ethane series; etc.

By polymerization, etc. Various compounds are converted to polymers or other products soluble in water or the reagent, leaving associates insoluble. An application of this principle is in the assay of the oil of cassia, the most important constituent of which is an aldehyd called cinnamaldehyd. On treating the oil with a strong solution of sodium bisulfite the cinnamaldehyd yields a product soluble in the reagent, while the other constituents (non-aldehyds) remain undissolved. The assay is conducted in a special flask of about 50 Cc. capacity, having a long neck holding about 6 Cc. and graduated into cubic centimeters and tenths. The oil and reagent are mixed in the flask, then water poured in until the non-aldehyds have risen into the neck where their volume is measured.

Other applications are for the determination of turpentine in the commercial article (*q. v.*), and nitrobenzene in commercial benzene by nitrification.†

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* Amer. Annual of Photography, 1898—72.

† Journ. Socy. Chem. Ind. 1884—74.

CHLORIMETRY.

In the older processes for the manufacture of bleaching powder, chlorine is generated by the action of hydrochloric acid (from sodium chloride and sulfuric acid) on a superoxide of manganese, and conducted over calcium hydrate. The manganese superoxide is either the native ore, consisting of the minerals wad, pyrolusite, etc., with more or less gangue, or the manganic hydrate regenerated from the spent manganese chloride (Weldon's mud) by precipitation by lime in contact with air.

The percentage of metallic manganese in an ore is, in this connection, a matter of indifference to the bleach-maker, he is simply wishing information as to what volume of chlorine will be furnished by a ton of a given ore. The weight of chlorine evolved is in the ratio of two atoms of chlorine to one atom of available oxygen in the ore,

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + 2Cl. \quad 1.227 \text{ lbs. yields 1 lb. Cl.}$$
$$Mn_2O_3 + 6HCl = 2MnCl_2 + 3H_2O + 2Cl. \quad 2.228 \text{ " " " "}$$
$$Mn_3O_4 + 8HCl = 3MnCl_2 + 4H_2O + 2Cl. \quad 2.327 \text{ " " " "}$$

Since the ores are generally mixtures of the different oxides and contain sand, clay, etc., every purchase must be tested to ascertain its chlorine value. Moreover there are occasionally associated with the manganese superoxide certain minerals of a reducing nature soluble in hydrochloric acid or the acid plus chlorine, and that proportionally reduce the yield of chlorine. Thus, taking as an extreme case a mixture of magnetite ($Fe_2O_3.FeO$) and hausmannite (Mn_3O_4) in the molecular proportion of two to one — that is containing 66.97 per cent of magnetite and 33.03 per cent of hausmannite — there is contained 2.31 per cent of available oxygen; but the manufacturer on heating the mixture with hydrochloric acid will obtain no chlorine whatever (theoretically), since

$$Mn_3O_4 + 2Fe_3O_4 + 24HCl = 3MnCl_2 + 3Fe_2Cl_6 + 12H_2O.$$

All the analytical methods hitherto proposed are based on the principle of measuring the oxidizing power of the available oxygen, by its direct or indirect reaction with a known weight of a reducer and determining the excess of the latter. The following are in common use:

1. Pattinson's. The finely powdered ore, dried at 110°, is placed in a small flask and dissolved in a warm mixture of a specified volume of standard ferrous sulfate with sulfuric acid, when the reactions

$$MnO_2 + 2FeSO_4 + 2H_2SO_4 = MnSO_4 + Fe_2(SO_4)_3 + 2H_2O.$$
$$Mn_2O_3 + 2FeSO_4 + 3H_2SO_4 = 2MnSO_4 + Fe_2(SO_4)_3 + 3H_2O.$$
$$Mn_3O_4 + 2FeSO_4 + 4H_2SO_4 = 3MnSO_4 + Fe_2(SO_4)_3 + 4H_2O.$$

take place, each atom of available oxygen in the ore changing two atoms of ferrosum to ferricum. When the reaction is over the excess of ferrous sulfate is determined by titration by standard permanganate, and the available oxygen and corresponding chlorine calculated.

Throughout the experiment the ferrous sulfate is protected from oxidation by the air by transmission of a current of carbon dioxide through the flask. Or the flask may be closed by a cork from which passes an open glass tube

doubly bent, the exit dipping into water; the air originally in the flask is displaced by carbon dioxide by the admixture of a little sodium bicarbonate with the ore, this reacting with the acid before the ore is attacked.

A grave objection to the above method is the use of dilute sulfuric acid as the solvent in which magnetite and other reducing mineral compounds are not readily soluble; and though the process be modified by the substitution of hydrochloric acid for sulfuric (and potassium bichromate for permanganate), still there is lacking the aid of the powerful oxidizer free chlorine. Taking the above example of the mixture of magnetite and hausmannite, if *all* the magnetite dissolves in the sulfuric acid the result will correctly indicate *no* available oxygen in the mixture and no chlorine would be evolved in practice, since

$$Mn_3O_4 + 2Fe_3O_4 + 12H_2SO_4 + (FeSO_4) = 3MnSO_4 + 3Fe_2(SO_4)_3 + 12H_2O + (FeSO_4).$$

the ferrous sulphate remaining entirely unoxidized. But if *none* of the magnetite dissolved, the result would show the whole of the available oxygen of the hausmannite. As only a part, and perhaps only a small part, of the magnetite would dissolve, the result would be in so far misleading.

2. Bunsen's method. The error referred to in (1) is not incurred in the method of Bunsen which imitates the process of the manufacture of chlorine on a large scale, and furnishes corresponding results.

The powdered ore in a small flask is boiled with concentrated hydrochloric acid and the evolved chlorine led through a solution of potassium iodide. The chlorine displaces an equivalent of iodine according to the equation $2KI + Cl_2 = 2KCl + I_2$. The freed iodine, held in solution by the excess of potassium iodide, is titrated by a standard solution of sodium thiosulfate with starch-paste as indicator — $I_2 + 2Na_2S_2O_3 = NaI + Na_2S_4O_6$. The excess of potassium iodide does not interfere with the titration. The end-point is shown by the breaking up of the intensely blue iodide of starch ($(C_{24}H_{40}O_{20}I)_4HI$?) and the consequent decolorization of the solution. From the weight of the liberated iodine is calculated that of the chlorine.

DeKoninck and Lecruer* assert that in the process as carried out on these lines, much hydrochloric acid vapor passes into the solution of potassium iodide and forms therein hydriodic acid which is readily decomposed by air with the liberation of iodine. They prefer to mix the ore with two or three parts of water and pass into the mixture and through the absorbent, in succession, carbon dioxide, gaseous hydrochloric acid, and carbon dioxide.

3. Fresenius and Will's method. Oxalic acid is decomposed to carbon dioxide and water by a higher oxide of manganese; *e. g.*, the binoxide —

$$MnO_2 + H_2C_2O_4 = MnO + H_2O + 2CO_2; \text{ or}$$
$$MnO_2 + H_2C_2O_4 + H_2SO_4 = MnSO_4 + 2H_2O + 2CO_2 —$$

the other superoxides reacting in a similar way.

The ore is placed in the flask A, Fig. 2, and covered with dilute sulfuric acid. An excess of solution of oxalic acid is poured into B, and D is half filled with concentrated sulfuric acid. The apparatus is weighed and the oxalic solution run into the flask; the liberated carbonic acid passes out through D, dried meanwhile by the sulfuric acid. When the reaction is over the liquid in the flask is boiled and a current of dry air drawn through, entering at B and leaving at D, to remove the last traces of carbon dioxide from the solution. The apparatus is cooled and reweighed, the loss from the preceding weight being carbon dioxide, from which the weight of available oxygen can be calculated by the above equations.

* Chem. News, 1891—1—230.

A modification, somewhat more accurate, is to determine the volume of carbon dioxide by measuring it in a nitrometer, Fig. 118.

4. Baumann applies the reaction of hydrogen peroxide for the determination, one atom of available oxygen from the manganese superoxide uniting with one atom of oxygen from hydrogen peroxide to form a molecule; thus with manganese sesquioxide —

$$Mn_2O_3 + H_2O.O = 2MnO + O_2 + H_2O.$$

The oxygen formed may be determined in two ways; gravimetrically, by the loss in weight when the operation is done in a weighed flask as in Fresenius and Will's method *supra;* or volumetrically, by acting on the superoxide by a known volume (an excess) of standard solution of hydrogen peroxide, then titrating back the excess by standard permanganate.

In Weldons mud there are contained besides manganese superoxides, the oxides of calcium and other bases which generate no chlorine when the mud is dissolved in hydrochloric acid, though using up their equivalents of acid. For their determination a weighed amount of the mud is heated with a known volume, an excess, of normal oxalic acid. The acid reacts with the manganese binoxide to form manganous oxalate — $MnO_2 + 2H_2C_2O_4 = MnC_2O_4 + 2H_2CO_3$ — this requiring two equivalents of oxalic acid for one of manganese binoxide. The other bases also form oxalates. An aliquot part of the filtered solution is titrated by normal sodium hydrate and phenol-phthalein. Deducting two equivalents of acid for the manganic oxide (whose amount has been previously found) the remainder is the oxalic acid required for the other bases, from which may be calculated the corresponding weight of hydrochloric acid required for their solution. *

For the determination of the chlorine and hydrochloric acid in the gases from the chlorine generator, a simple method is to pass five liters through a solution of pure caustic soda by which both are absorbed — $2Cl_2 + 4NaOH = 2NaOCl + 2NaCl + 2H_2O$; and $HCl + NaOH = NaCl + H_2O$. On titrating the solution by standard arsenious acid — $2NaOCl + As_2O_3 = 2NaCl + As_2O_5$ — each atom of the oxygen of the hypochlorite corresponds to two atoms of the chlorine in the gas. The total chlorine is determined by titration by standard silver nitrate. A simple calculation gives their respective proportions.

Another method is due to Younger. The gas is drawn into an aspirator bottle having a gauge showing the volume of gas entering it expressed in both cubic centimeters and in cubic feet and decimals. Before entering the aspirator the gas is passed through a wash bottle in the form of a long (20 inches) tube, containing 100 Cc. of a solution of arsenious acid, the reagent in the solution being an amount to exactly fix one gram of chlorine — ($As_2O_3 + 2Cl_2 + 2H_2O = As_2O_5 + 4HCl$); the solution also contains a little sulfate of indigo whose blue color is bleached by free chlorine.

The gas is drawn slowly through the wash-bottle until the indigo is just decolorized, showing that all the arsenious acid is oxidized. The aspirator is closed and the volume of gas drawn in is read in cubic feet. If exactly one cubic foot, for example, then the gas contains 15.432 grains (one gram) of chlorine per cubic foot, and other volumes proportionally.

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* Lunge, Chemische-technische Untersuchung, 430.

To determine the hydrochloric acid in the gas, ten Cc. of the solution in the wash-bottle is drawn out by a pipette and titrated by decinormal silver nitrate; this is tantamount to titrating the entire 100 Cc. with normal silver nitrate. The excess of silver solution required for precipitation over 28.2 Cc. is due to the hydrochloric acid in the gas, and the proportion may be readily calculated. The figure 28.2 is the volume of silver solution required to combine with the 4HCl liberated in the oxidation of the arsenious acid as shown in the above equation; *i. e.*, as one Cc. of normal silver nitrate is equivalent to .036458 gram of HCl, then 28.2 Cc. are equivalent to 1.028 grams of HCl, the amount formed by the hydrogenation of one gram of chlorine.

Between the wash-bottle and aspirator is interposed a tube containing a solution of potassium iodide. As soon as any chlorine passes the wash-bottle it liberates iodine which colors the solution yellow, thereby furnishing an indication in addition to that of bleaching the indigo.

BLEACHING POWDER.

The formula of this material is variously stated by different authorities; it is essentially a mixture of calcium hypochlorite with calcium chloride and a little calcium chlorate. Its commercial value as a bleach depends on the proportion of loosely combined chlorine of the hypochlorite.* Theoretically, assuming the formula $Ca_3H_6O_6Cl_4$, it contains about 39 per cent of the element in this state, a good commercial quality, when fresh, from 32 to 37 per cent.† It slowly decomposes on keeping, with loss of available chlorine. As a bleaching agent calcium chloride is of no value; nor is the chlorate, and the method adopted for the determination of available chlorine should differentiate between that from the hypochlorite and that formed by the action of the reagents on the chlorate.

To prepare the powder for analysis it is ground in a mortar with cold water, allowed to settle for a moment, and the turbid liquid poured into a liter flask. The coarser grains remaining in the mortar are again triturated and lixiviated as before, and the operation continued until all has been transferred, when the liquid is made up to the mark with water. Before taking out any part of the contents of the flask for analysis, a thorough shaking up is necessary, since the insoluble matter retains a little chlorine.

As in the analysis of manganese ores, all the methods measure the oxidizing power of the chlorine by means of a reducing agent, but here the measurement may be done (1), directly, or (2), by a determination of the excess of the reducer.‡

In the former class is an old, now discredited method directing to mix with the solution of bleaching powder a solution of ferrous chloride in hydrochloric acid, and throw in a weighed piece of copper. The mixture is boiled in a bask for some time without access of air. The reaction $CaOCl_2 + Cu_2 + 2HCl = CaCl_2 + Cu_2Cl_2 + H_2O$ ensues, the ferrous chloride acting only as a carrier of oxygen. The loss in weight of copper represents an equivalent of available chlorine in the powder.

Penot's method is based on the principle that an arsenite is oxidized to an arseniate by chlorine, and also that if a mixture of starch and potassium iodide is touched with a solution containing free chlorine the mixture becomes blue from the combination of starch with the iodine liberated from the iodide. To

* Biederman, Chem. Kal. 308.
† Journ. Anal. App. Chem. 1892—231.
‡ Chem. News, 1892—2—114.

the bleaching powder suspended in water, is added from a burette a standard solution of sodium arsenite, testing a drop of the fluid after each addition by allowing it to fall on paper coated with a mixture of starch and potassium iodide. When no color is produced it is known that all the available chlorine has reacted with the arsenite.

Another method is almost identical with that of Pattinson for the analysis of a manganese superoxide. The powder is treated with sulfuric acid and an excess of a standard solution of ferrous sulfate, and the unoxidized iron titrated by permanganate or bichromate. Here the chlorate also oxidizes an equivalent of iron.

Lunge takes advantage of the reaction between calcium hypochlorite and hydrogen peroxide — $CaOCl_2 + H_2O_2 = CaCl_2 + H_2O + O_2$ or $CaO_2C_2 + 2H_2O_2 = CaCl_2 + 2H_2O + 2O_2$. The bleaching powder is mixed with a solution of hydrogen peroxide in water in a nitrometer (page 144) and the evolved oxygen measured, its weight calculated, and the result converted to chlorine — one atom of oxygen corresponding to one atom of chlorine.

When potassium iodide and hydrochloric acid are added to bleaching powder, the chlorine liberates an equivalent of iodine which may be immediately titrated by sodium hyposulfite and starch paste, or better, by an excess of hyposulfite and back with iodine.

Of all the methods proposed, that of Penot is probably the most used, since arsenious acid (the solution of bleaching powder being normally alkaline) is not acted on by calcium chlorate, unlike many of the other reducing agents. For a separate determination of the calcium chlorate the following may be outlined: —

1. The chlorate is calculated from the difference between the result given by the method of Penot (*i.e.*, the available chlorine in the hypochlorite), and the result from some other method that measures the oxidizing power of both the hypochlorite and chlorate. Another plan is to titrate the solution of the powder by arsenious acid in both alkaline and acid solutions; in the former the arsenious acid is acted on but slowly by the chlorate, practically not at all during a titration, while an acid solution of a chlorate readily oxidizes it in a warm liquid.

2. Dreyfuss first treats the solution of the bleaching powder with a slight excess of ammonia. The hypochlorite is decomposed to calcium chloride, while the chlorate is only transformed to ammonium chlorate —

$$3CaOCl_2 + 2NH_3 = 3CaCl_2 + 3H_2O + N_2; \text{ and}$$
$$Ca(ClO_3)_2 + 2NH_4OH = 2NH_4ClO_3 + Ca(OH)_2.$$

the solution is then evaporated until the excess of ammonia is dissipated, and made up to a definite volume.

Of a standard solution of cupric sulfate, a measured volume is titrated by a solution of stannous chloride in hydrochloric acid, —

$$2CuSO_4 + 4HCl + SnCl_2 = Cu_2Cl_2 + SnCl_4 + 2H_2SO_4,$$

the end point shown by the discharge of the blue color. The liquid is now essentially a solution of pure cuprous chloride.

An aliquot part of the bleaching powder solution prepared as above is added to the cuprous chloride solution; the ammonium chlorate reacts to form cupric chloride —

$$3Cu_2Cl_2 + NH_4ClO_3 + 6HCl = 3Cu_2Cl_4 + NH_4Cl + 3H_2O.$$

The solution is once more titrated by the stannous chloride solution till colorless to determine the amount of cupric chloride formed, from which the amount of chlorate is calculated. To standardize the stannous chloride solution, a similar experiment is made on pure potassium chlorate.

3. Fresenius* directs to mix the aqueous extract of the powder with neutral lead acetate solution in excess. A precipitate falls, a mixture of lead chloride and lead hydroxide. The hypochlorite slowly reacts with the lead chloride — $2CaOCl_2 + PbCl_2 = PbO_2 + 2CaCl_2 + Cl_2$; later the chlorine reacts with the excess of lead acetate — $Cl_2 + 2Pb(C_2H_3O_2)_2 + 2H_2O = PbCl_2 + PbO_2 + 4HC_2H_3O_2$. The liquid is filtered and the filtrate concentrated. The calcium chlorate, not decomposed in the preceding reactions, is determined by acidulating the filtrate by hydrochloric acid, distilling the liberated chlorine ($(CaClO_3)_2 + 12HCl = CaCl_2 + 6Cl_2 + 6H_2O$) into potassium iodide, and titrating by thiosulfate the iodine set free.

Eau de Javelle is essentially a solution of sodium hypochlorite in water. It has normally an alkaline reaction due to sodium hydrate and carbonate, and it is sometimes desirable to determine these constituents. The sodium hydrate may be titrated directly by a standard acid and phenol-phthalein; the red color persists as long as free alkali remains, but is then immediately bleached by the free chlorine, ($NaOCl + 2HCl = NaCl + Cl_2 + H_2O$). Since chlorine is temporarily liberated throughout the titration, several additions of minute amounts of the indicator are made while the titration is in progress.

Or the oxygen of the hypochlorite may be eliminated by heating the *eau* with a slight excess of ammonia — $3NaOCl + 2NH_3 = 3NaCl + N_2 + 3H_2O$. After evaporating until the excess of ammonia has been expelled the liquid is titrated by normal acid and methyl orange, or first by phenol-phthalein, then by methyl orange (page 121). The reaction with ammonia has also been applied for the determination of available chlorine in bleaching powder, measuring the nitrogen evolved.

Another way to decompose the hypochlorite is by treatment with precipitated cobalt sesquioxide or nickel sesquioxide suspended in water. Sodium chloride and the protoxide of the metal are formed, the free alkali and alkali carbonate remaining unchanged — $NaOCl + Co_2O_3 = NaCl + 2CoO + O_2$.

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* Zeits. angew. 1895—501.

IRON AND STEEL.

The chemical reactions involved in the processes of smelting and refining these metals are so well comprehended that quite an effective control of the character of the products is permitted, and there is maintained at every large works a laboratory for the systematic examination of the raw materials and products and by-products. From the analytical data in conjunction with mechanical tests, the details of the processes of manufacture are modified, aiming at the production of the largest output of the best quality for the specific purpose intended, and at the lowest cost.

Pig iron and steel are essentially iron containing small proportions of carbon, sulfur, silicon, and phosphorus, and sometimes copper, titanium, arsenic, nickel, etc., and alloyed with a little manganese. The state in which the nonmetallic elements exist — whether chemically combined with iron or manganese or with each other, or simply dissolved in the matrix of iron — is as yet a matter of controversy; and while the influence of carbon on the physical properties of iron is fairly well known, the effect of the other elements usually contained, though quite as pronounced, is more obscure and can only be traced in a general way.

Pig iron and cast iron contain much larger proportions of carbon and silicon than the refined metals, part of the carbon being in the free state (graphitic carbon, graphite, kish). The difference in composition between the various grades of raw and refined metals can be seen in the following analyses of typical specimens; however, the percentages often vary largely from the figures here given.

It will be noticed that the percentages of combined carbon and manganese are greater in the white pig iron than in the gray, while the graphite and silicon are less; the mottled iron is intermediate. Also that in the milder grades of steel (those comparatively low in carbon) the percentages of the constituents closely approach those in wrought iron. From the composition alone it is often impossible to state positively that a given sample is mild steel or wrought iron, though as a rule the percentage of manganese is higher and the phosphorus and sulfur lower in the former. The percentage of slag and oxides, character of the fracture shown on breaking by tension or transversely, and the microscopical appearance of a slightly etched plane surface afford evidence as to the method of manufacture.

	Combined carbon.	Graphite.	Silicon.	Sulfur.	Phosphorus.	Manganese.	Iron. etc.
A.	2.45	1.46	2.23	.09	.21	.35	93.21
B.	2.92	1.20	1.12	.08	.16	.40	94.12
C.	3.37	.35	.42	.11	.17	.61	94.97
D.	4.22	.18	1.06	.01	.13	22.15	72.25
E.	6.78	trace.	2.28	—	.28	79.76	10.90
F.	.10	.06	.16	.15	.17	.22	99.14
G.	.11	—	.01	.08	.07	.43	99.30
H.	.18	—	.03	.02	.03	.25	99.49
I.	.55	—	.12	.07	.09	1.00	98.17
J.	1.05	—	.15	.05	.06	.42	98.27

A. Gray pig iron for founding.
B. Mottled pig iron for founding.
C. White pig iron for making wrought iron.
D. Spiegel-eisen (manganiferous pig iron), "22 per cent."
E. Ferro-manganese (ferriferous manganese), "80 per cent."
F. Wrought iron, of fair quality.
G. Bessemer steel, for wire.
H. Open hearth steel, for boiler plate.
I. Bessemer steel, for railroad rails.
J. Open hearth steel, for tools, moderately hard.

An outline of the processes of smelting iron ore and the manufacture of steel and wrought iron may be of interest.

1. For the manufacture of pig iron, calculated weights of iron ore, coke and limestone are in turn charged into a tall cylindrical furnace supplied with heated air blown in through tuyeres near the bottom. At the region of the tuyeres coke burns to carbon dioxide ($C + O_2 = CO_2$); the gases passing upward meet incandescent coke, and the carbon dioxide is reduced to carbon monoxide ($CO_2 + C = 2CO$). The carbon monoxide reacts with the iron ore to produce metallic iron ($Fe_2O_3 + 3CO = Fe_2 + 3CO_2$), and also to a limited extent with the silica of the gangue of the ore to form silicon ($SiO_2 + 2CO = Si + 2CO_2$); similarly the phosphoric acid and sulfur trioxide of the ore and coke are reduced to phosphorus and sulfur.

The metallic iron, in intimate contact with finely divided carbon, alloys with about four per cent of this element and the silicon, phosphorus, and part of the sulfur, and melts, finally dropping into the reservoir (crucible) at the bottom of the furnace, where it collects, protected by a layer of specifically lighter slag from oxidation by the blast, and is tapped out periodically.

The object of the limestone is to flux the gangue of the ore (sand, clay, etc.) and the ash of the coke, these being infusible at furnace temperatures. In contact with lime there is formed a comparatively easily fusible slag, a complex silicate of lime, alumina, magnesia and manganese protoxide, containing a small amount of calcium sulfide.

The gas arising to the top of the furnace is a mixture of carbon monoxide, carbon dioxide (partly from the limestone) and nitrogen (from the air). It is combustible and therefore carried down to be burned in the regenerative stoves used to heat the air-blast entering the tuyeres.

2. Wrought iron is made from pig iron, preferably of the white or mottled grades. A charge of iron is melted in a horizontal furnace whose bed is made of a pure variety of iron ore. Through the action of the iron oxide and the air the silicon and manganese of the pig iron are gradually oxidized, and to a great extent the phosphorus and sulfur, the carbon burning to carbon monoxide. The ferric oxide of the bed is partially reduced to ferrous oxide which unites with the silica, manganese oxide, and phosphoric acid to form an easily fusible slag. As the pig iron gradually loses its carbon and silicon it becomes proportionately less fusible, and finally comes to the form of a pasty mass inclosing considerable of the slag. The mass is divided into several parts which are gathered into balls and each ball subjected to extensive mechanical treatment (squeezing, hammering and rolling) at a high heat to expel the slag. The product is wrought iron, graded according to the quality of the original pig iron and the extent of mechanical working the product has undergone.

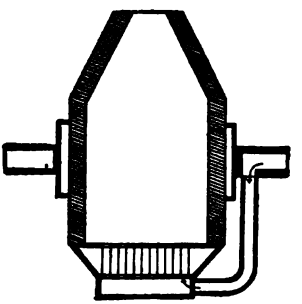

Fig. 172. $^1/_{160}$

3. Acid Bessemer steel is made in a converter shown in section in Fig. 172, lined with a mixture that is essentially silica. In the bottom are numerous small holes through which enters air under high pressure. The converter being partly filled with melted pig iron, the air forces its way upward through it, the oxygen converting an equivalent of iron into protoxide. The protoxide immediately reacts, first with silicon to form silica ($Si + 2FeO = SiO_2 + Fe$); later with manganese ($Mn + FeO = MnO + Fe$); and finally with carbon ($C + FeO = CO_2 + Fe$). During the oxidation of these elements a brilliant flame emerges from the converter, suddenly ceasing when oxidation is complete; at or just before this moment the converter is turned to a horizontal position and the blast shut off.

The metal in the converter is now nearly pure iron containing considerable ferrous

oxide, and covered by a thin layer of slag, a silicate of ferrous oxide, manganese oxide, and the earths (from the lining principally). To it is added a suitable proportion of melted spiegel-eisen (an alloy of manganese, iron and carbon), for three purposes; (1), a part of the manganese reacts with the ferrous oxide converting it to iron ($FeO + Mn = Fe + MnO$), the manganese oxide passing into the slag; (2), the remainder of the manganese alloys with the metal; it has a beneficial influence on the quality of the steel; and (3), the carbon enters the metal conferring the desired hardness. The steel is now poured into ingot molds.

4. The manufacture of acid open-hearth steel is based on three propositions. (1) When pig iron and wrought iron of suitable qualities and in the proper relative proportions found by calculation, are melted together, the product conforms chemically to the composition of steel. (2) As in the Bessemer process, when melted pig iron is exposed for some time to a current of air the carbon, silicon, and manganese are oxidized and eliminated, until at a certain stage the composition is that of steel. (3) The same effect as in (2) transpires when pig iron and iron oxide (iron ore) are melted together, the oxygen being supplied by the ore. In current open-hearth practice the three are combined.

Pig iron, scrap wrought iron, and iron ore in suitable proportions are together charged into the open-hearth furnace, of which one form is that of a horizontal cylinder lined with a mixture of silica and fire-clay. A gas flame enters, alternately at one end and the other, heating the upper part of the lining. The charge is melted by radiated heat. The silicon, manganese, and carbon of the pig iron are lessened in percentage in the total amount of metal (pig iron plus wrought iron) as in (1), and almost entirely eliminated by oxidation as in (2) and (3). The metal has now become practically pure iron containing a small proportion of ferrous oxide, and is converted to steel by the addition of high grade spiegel-eisen (ferromanganese) as in the Bessemer process.

The distinction between the 'acid' and 'basic' Bessemer and open-hearth processes lies in the composition of the slag formed therein. In the acid processes the silica of the slag is largely in excess of the bases, and conversely. In the acid process the phosphorus of the pig iron is continually oxidized to phosphoric acid and unites with ferrous oxide, but is as continually displaced by silica and reduced back to phosphorus again to return to the metal; so that the resulting steel contains practically all the phosphorus of the pig iron. In the basic processes the phosphorus is oxidized, and the phosphoric acid unites with lime and enters and remains permanently in the slag, and hence a pig iron high in phosphorus and correspondingly low in price can be used to make low-phosphoric steel. The linings of the converter and open-hearth furnaces are mainly silica for the acid process; and for the basic, magnesia, lime and magnesia, or a neutral material such as carbon or chrome iron ore, with addition of limestone to the charge.

Steel and the softer irons are prepared for analysis by drilling the metal with a clean twist-drill, using no water or oil; filing is not to be recommended as more or less foreign matter is apt to be mixed with the filings. Since the drillings of soft pig iron are made up of light scales of graphite with much heavier fragments of iron, a perfect mixture for the determination of carbon, etc., can only be secured by moistening the whole of the drillings with pure alcohol, dividing down the paste to the weights desired for the determinations, and drying.

The harder grades of pig iron, chilled iron, spiegel-eisen, ferro-manganese and quenched steel are broken to a coarse powder in a steel mortar.

Before considering the methods of analysis in detail, let us examine the action of the various common solvents on the metals and their impurities. With the exception of a few of the rarer alloys all the commercial grades of iron and steel are soluble in dilute mineral acids and in concentrated hydrochloric acid. For the determination of manganese, silicon, copper and other impurities that form no volatile compounds with hydrogen, any acid may be the solvent, while phosphorus and sulfur are retained in solution only by an oxidizer such as nitric acid or bromine in hydrochloric acid. Special solvents effect the separation of iron and manganese from combined or dissolved carbon.

1. Hydrochloric acid, both concentrated and dilute, dissolves manganese to manganous chloride, and iron to ferrous chloride; but unless precautions are taken against contact of the air some ferric chloride also is formed. The combined (or dissolved) carbon for the most part unites with nascent hydrogen and passes off as odorous gases said to be of the propyl series; a small proportion, less if the solvent be heated, separates in the solid form. The graphitic carbon remains undissolved. The combined silicon is oxidized, and more or less passes into solution according to the strength of acid, temperature, etc., while crystallized and graphitoid silicon remain. A part, usually the greater part, rarely the whole, of the sulfur combines with nascent hydrogen and passes off as hydrogen sulfide: the remainder is left in the residue of graphite, etc., possibly as an organic compound, possibly as iron disulfide. Of the phosphorus, part passes off as gaseous hydrogen phosphide, the proportion varying with the percentage of carbon in the metal; part enters the solution as phosphoric acid; and part remains in the insoluble residue. When iron containing a large percentage of phosphorus is dissolved in dilute hydrochloric acid there is left a black residue said to be composed of iron, phosphorus, hydrogen, oxygen, and water.

Of the other elements, copper remains in the metallic state; titanium is also left, probably as titanium carbide; while manganese oxide, ferrous oxide and slag are dissolved. The above statements are to be accepted as true only in a general way, since the nature and proportions of the associates influence the solubility.

2. Dilute sulfuric acid is similar in action to hydrochloric but is somewhat inferior in solvent power and the reactions are less sharp and complete. There is less ferric compound formed with an equal exposure to the air than where the solvent is hydrochloric acid.

3. Hot concentrated sulfuric acid and melted sodium pyrosulfate attack the finely divided metals, and on dilution with water the sulfates dissolve, leaving silica and graphite. These reagents are seldom used however.

4. A mixture of hydrofluoric with one of the mineral acids has the effect of taking silica into solution and the liquid does not gelatinize on standing or evaporation (hindering filtration), and for some determinations on siliconiferous pig irons saves an evaporation to dryness to render silica insoluble.

5. Cold concentrated nitric acid causes iron to become passive and no further action ensues. On boiling the acid the metal is slowly dissolved, the sulfur being converted entirely to sulfuric acid; this is about the only occasion for the use of nitric acid of this strength.

6. Nitric acid of moderate dilution dissolves iron to ferric nitrate and manganese to manganous nitrate; some samples of pig iron become passive in the cold acid of a gravity of 1.2. The combined carbon dissolves on heating to a clear brown solution, the graphite remaining unacted on. Silicon partly passes into solution as hydrated silica, the more the weaker the acid. Sulfur is converted to sulfuric acid provided the acid is in large excess and hot throughout the operation, otherwise some sulfur may remain as a fine powder suspended in the liquid or escape as sulfurous acid or hydrogen sulfide. The phosphorus is oxidized, mainly to phosphoric acid, and passes into solution. Copper dissolves as cupric nitrate, and arsenic as arsenic acid.

7. Aqua regia combines the solvent power of hydrochloric acid with the oxidizing effect of nitric, and has a few applications on this account.

8. A cold aqueous solution of bromine, chlorine, or iodine dissolves iron and manganese as halogen compounds, leaving the carbon and, more or less completely, the other impurities, including the slag and oxides. Similarly,

solutions of easily reducible per-salts such as ferric chloride, mercuric chloride, etc., are reduced, the iron and manganese assimilating the freed rest and passing into solution. Salts of copper and silver are decomposed, their metals being deposited while iron and manganese are dissolved; the double chloride of copper and an alkali metal first takes up the iron and manganese, at the same time depositing their equivalents of metallic copper; then the excess of the reagent dissolves the copper as cuprous chloride.

9. Cold dilute hydrochloric or sulfuric acid containing an oxidizing agent, such as chromic acid, dissolves the metal without the evolution of hydrogen, this being immediately converted into water by reacting with the chromic acid. The combined carbon is mainly left in the insoluble residue of graphite. Chromic acid in hot concentrated sulfuric acid acts energetically to oxidize all the carbon to carbon dioxide.

Silicon may be determined by dissolving the metal in hydrochloric acid, evaporating to thorough dryness, and redissolving the bases in nitric or hydrochloric acid. All the silicon is converted into insoluble silica which is filtered, ignited and weighed. It is seldom obtained pure, however, containing iron oxide, scale, etc. For purification it may be fused with a little sodium carbonate, the melt dissolved in hydrochloric acid, evaporated to dryness, the residue treated with dilute hydrochloric acid, and the silica, now pure, ignited and weighed. Another plan is to volatilize the silica by hydrofluoric acid, evaporate and weigh the residue; the loss in weight is silica.

In the method of Drown the pig iron or steel is dissolved in a mixture of dilute sulfuric and nitric acids and the solution evaporated until the excess of sulfuric becomes concentrated; at this point the silicon hydrate is dehydrated and soluble carbonaceous compounds oxidized. The residue is treated with hot dilute hydrochloric acid to dissolve the ferric and manganous sulfates, filtered, and the residue of graphite and silica ignited until the former has burned away. Pure silica is left. It is immaterial as regards accuracy as to whether the metal is originally dissolved in sulfuric or in nitric acid or as to the excess of either. But the plan of dissolving in dilute sulfuric acid and then oxidizing by nitric requires only about one-fourth of the volume of the latter as compared with the use of nitric as the solvent — a consideration in laboratories where many determinations are made daily.

For rapid determinations of silicon in iron from a blast furnace, the melted metal is run into cold water, solidifying in the form of chilled globules easy to pulverize in a steel mortar. The powder is dissolved in hot hydrochloric acid in a platinum dish, boiled to dryness, redissolved in acid, and filtered by suction. The paper and carbon are burned off in a current of oxygen. The results are only approximations, yet are close enough for the purpose — that of ascertaining the grade of iron and the state of the furnace — and can be reported in less than fifteen minutes from the time of catching the sample.

In the result of a determination of silicon in iron is included the silicon of any slag contained in the metal.

Slag and oxides of manganese and iron. These are general constituents of refined iron, but are in less amount in pig iron and steel. None of the methods for their determination can be considered satisfactory.

Various solvents have been proposed for the solution of the iron and manganese without the slag and oxides being attacked; such are aqueous solutions of iodine, bromine, ferric chloride, and simple and double salts of copper;

iodine dissolved in solution of potassium iodide or ferric chloride; certain metallic oxides suspended in water, etc. The residue left after treating the metal by one of these solvents is boiled with potash solution to dissolve free silica and carbon hydrates, the residue ignited to burn the graphite, and weighed as a mixture of slag and oxides. If considerable in amount, the silica contained may be determined by volatilizing it by hydrofluoric acid, and the proportion of slag calculated, knowing its approximate composition.

In Pourcel's method the metal is placed in a porcelain boat at the middle of a porcelain tube through which is passed a current of oxygen-free dry chlorine. The volatile ferric chloride formed is carried to the cooler parts of the tube, depositing as anhydrous golden-yellow flakes, the graphite, slag, oxides, etc, remaining in the boat.

Tucker* heats the powdered metal to fusion in a brasque clay crucible with exclusion of air; the button of metal is weighed, and the loss in weight is assumed to be the oxygen of the oxides which has combined with the carbon of the metal or the brasque, and escaped as carbon monoxide or dioxide. A correction is applied for carbon taken up by the metal from the brasque, found by determining the carbon in the metal before and after the operation.

Manganese. Here the difficult problem is to separate a large amount of iron from a small proportion of manganese — difficult, because in nearly all the accepted methods for their separation either the iron is precipitated as a compound of a voluminous flocculent form that can scarcely be washed completely, or the manganese as manganic oxide or hydrate, remarkable for their power of occluding the compounds of other metals.

1. Ammonia precipitates ferric hydrate from a ferric and manganous solution; theoretically all the manganese should remain in solution as a manganous ammonium salt, but this is true only when it is present in but a very small proportion and the solution very dilute, otherwise much accompanies the ferric hydrate.

2. Barium carbonate precipitates the iron from a neutral ferric solution as basic ferric hydrate mixed with the excess of the precipitant, most or all of the manganese remaining in solution. The filtrate is acidified, the barium that has gone into solution removed by sulfuric acid, and the manganese determined in the filtrate.

An excellent method where the proportion of manganese to iron is large is to neutralize the solution of ferric and manganous chlorides with sodium carbonate, then stir in a slight excess of pure lead carbonate, lead replacing the iron. The filtrate is acidified and treated with hydrogen sulfide to remove the lead, leaving only manganous chloride in solution.†

3. An acetic acid solution of nitroso-beta-napthol was proposed as a precipitant for ferric salts by von Knorre.‡ A neutral or faintly acid solution of a ferric salt yields a bulky brown compound, ferri-nitroso-napthol, $Fe(C_{10}H_6O.NO)_3$; manganese is not precipitated. In the filtrate the manganese is separated as binoxide by making the solution ammoniacal and passing a current of air loaded with bromine vapor.

4. On boiling a dilute neutral solution containing iron as a ferric salt, all the iron comes down as ferric hydrate, a manganous salt remaining

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* Journ. Iron & Steel Inst. 1881—205.

† Journ. Anal. Chem. 2—291.

‡ Chem. News, 1889—1—232.

undecomposed. The method is not much in use, for the reason that as the precipitation takes place in a neutral solution the manganese is held up less completely than in an acid solution, as in (5).

5. Of all the methods for material wherein the iron largely preponderates over the manganese and where the iron is precipitated for the separation, probably the best separation is afforded by the 'basic acetate' method. To the slightly acid solution of ferric and manganous chlorides or sulfates is added an excess of an alkali acetate (preferably the ammonium salt). On boiling the dilute solution all the iron precipitates as basic ferric acetate. Unfortunately the precipitate is so bulky and slimy that it is difficult to filter and impossible to thoroughly wash, and must be dissolved and reprecipitated one or more times for a complete separation. Succinnic acid is said by Fresenius to afford a precipitate denser and easier to wash.

A combination of the methods (4) and (5) is the addition of an insufficient proportion of acetate to transpose with all the iron and manganese chlorides. It is claimed that manganese acetate is readily decomposed on boiling, with formation of manganese hydrate; and that if less of the acetate be used than will convert all the iron to acetate, all the manganese will remain as chloride or sulfate. In this case the precipitation of the iron is due partly to the decomposition of the acetate and partly to the decomposition of a neutral solution. However, the distinction is not of importance if viewed by the dissociation theory.*

The basic acetate method is well suited to material containing much manganese with little iron, as in spiegels, ferro-manganese, and manganese ores. In such cases the separation may with advantage be preceded by a careful separation by ammonia to withdraw most of the manganese from the iron.

6. Of the few methods wherein the manganese is separated by precipitation leaving the iron in solution is the deservedly favored one due to Ford.† The metals are obtained as nitrates dissolved in strong nitric acid; on dropping crystals of potassium chlorate into the boiling solution, first the carbonaceous matter is oxidized, then the manganese precipitates as binoxide. The reaction is undoubtedly complex; perhaps the leading one is

$$5Mn(NO_3)_2 + 2KClO_3 + 4H_2O = 5MnO_2 + 2KNO_3 + 8HNO_3 + Cl_2.$$

Nearly all the iron is left in solution. For several reasons it is better to filter without dilution, so the liquid is passed through an asbestos felt or sand filter. After washing with colorless concentrated nitric acid, then with water, the precipitate is dissolved in sulfurous or hydrochloric acid. As a small amount of ferric nitrate is invariably carried down mechanically, it is removed by a basic acetate separation.

Ford's method is well adapted to material in which the proportion of iron exceeds that of manganese, but where manganese preponderates, the basic acetate method is preferable for some reasons.

7. Rothe ‡ proposes a separation based on the solubility of ferric chloride in ether and the insolubility of manganous chloride. The solution of the chlorides of the two metals is made slightly acid and extracted by ether in a special form of apparatus; the same procedure is followed as for the extraction of an organic body from an aqueous solution.

8. Blum § describes a method based on the precipitation of manganese from

* Chem. News, 1873—1—14 and Journ. Anal. Appl. Chem. 1892—94.
† Trans. Amer. Inst. Mining Engrs. 9—397.
‡ Mitth. d. Vers-Anst. 10—123.
§ Chem. News, 1887—1—236.

an ammoniacal solution of ferric and manganous tartrates by potassium ferrocyanide.

The separation having been accomplished by one of the above methods, the manganese may be determined by precipitation either as the binoxide or as the ammonium phosphate. For the former the solution is nearly neutralized by ammonia, ammonium acetate and bromine added, then an excess of ammonia, and the solution boiled for a time. The manganese precipitates as manganic hydrate —

$$Mn(C_2H_3O_2)_2 + 5Br + 8NH_3 + H_2O = MnO_2xH_2O + 5NH_4Br + 2NH_4C_2H_3O_2 + N.$$

After filtering and washing with very slightly acidulated water, the precipitate is strongly ignited and weighed as Mn_3O_4, though its composition may vary somewhat in the ratio of manganese to oxygen.

The second form is the better; the solution is treated hot with ammonium phosphate and ammonia (page 243), and after ignition the precipitate is weighed as manganese pyrophosphate.

Volumetric methods. All these depend on the formation of a definite oxide of manganese higher than the protoxide, the determination of the active oxygen therein by means of a standard solution of some reducing agent, and calculation of the manganese from the atomic ratio.

1. Pattinson's. The hot solution, containing the iron as ferric chloride, is neutralized and treated with calcium carbonate and bromine or calcium hypochlorite, giving a precipitate of ferric and manganic hydrates. After filtration and washing, the precipitate is treated with dilute sulfuric acid and a measured volume of ferrous sulfate solution. The sulfuric acid dissolves the ferric hydrate to ferric sulfate, and the acid and ferrous sulfate dissolve the manganic hydrate to manganous sulfate, an equivalent of ferrous iron being converted to ferric. The excess of ferrous sulfate is found by titration by standard permanganate, and from the iron oxidized, the weight of the manganese. Assuming the manganic hydrate to have the formula $MnO_2.xH_2O$, the reactions are

$$MnCl_2 + 2CaCO_3 + 2Br + 2H_2O = MnO_2 + CaCl_2 + CaBr_2 + 2H_2CO_3.$$
$$MnO_2 + 2FeSO_4 + 2H_2SO_4 = MnSO_4 + Fe_2(SO_4)_3 + 2H_2O.$$
$$10FeSO_4 + K_2Mn_2O_8 + 8H_2SO_4 = MnSO_4 + Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O.$$

Hydrogen peroxide has been recommended for the oxidizing agent, but it is doubtful if the precipitate always has a constant composition.

2. Vortmann treats the solution with potassium hydrate and a measured volume, an excess, of decinormal iodine solution; the iron precipitates as ferric hydrate, and the manganese as peroxide —

$$MnCl_2 + I_2 + 4KOH = MnO_2 + 2KCl + 2KI + 2H_2O.$$

After diluting to a certain volume and filtering, an aliquot part of the filtrate is acidified and the iodine in excess titrated back by decinormal sodium thiosulfate and starch-paste.

3. In Troilius' method the manganese is precipitated alone by potassium chlorate as in Ford's method. After filtering through asbestos and washing, the precipitate is dissolved in excess of standard solution of ferrous sulfate and sulfuric acid, and the excess of ferrous iron titrated back by potassium bichromate. Modifications of the method are due to Williams,* who substitutes oxalic acid for the ferrous sulfate and potassium permanganate for the bichromate

$$MnO_2 + H_2C_2O_4 + H_2SO_4 = MnSO_4 + 2H_2CO_3;$$

* Trans. Amer. Inst. Mining Engrs. 10—100.

by Julian,* who omits the filtration and dissolves the binoxide in the diluted nitric solution with a standard solution of hydrogen peroxide, titrating its excess with permanganate; and by Smith, who treats the residue with an excess of hydrogen peroxide and measures the evolved oxygen.

4. Volhard's † method is based on the principle that zinc is intermediate in chemical potential between iron and manganese. The sample is dissolved in nitric acid, evaporated with sulfuric acid, and the sulfates dissolved in water and filtered if necessary. In the cold solution the iron is precipitated by zinc oxide,

$$Fe_2(SO_4)_3 + 3ZnO + 3H_2O = Fe_2(OH)_6 + 3ZnSO_4,$$

leaving the manganese in solution. After making up to a definite volume and filtering, an aliquot part of the filtrate is treated with a drop of nitric acid (to destroy traces of organic matter), heated to near boiling, and titrated by standard permanganate; both the manganese of the manganous sulfate and that of the permanganate are converted into insoluble manganic oxide,

$$6MnSO_4 + 2K_2Mn_2O_8 + 4H_2O = 10MnO_2 + 4KHSO_4 + 2H_2SO_4.$$

The end of the titration is shown by a persistent faint pink color of the solution from a slight excess of permanganate.

The process is simplified by Sarnstroem, who adds a slight excess of sodium bicarbonate to the acid solution of ferric and manganous chlorides: the iron precipitates as ferric hydrate and the manganese stays in solution. The titration is made without filtering off the ferric hydrate, as its presence is an advantage in clarifying the solution during titration.

All these volumetric methods give slightly low results. The cause has been ascribed to (1) that not the binoxide as assumed, but some lower oxide or mixture of oxides (*e. g.*, $Mn_{10}O_{19}$) forms the precipitate;‡ (2) the manganese binoxide as it forms occludes some unprecipitated manganous nitrate which, of course, has no oxidizing action on the ferrous solution; or (3) manganese binoxide reacts with manganous nitrate to form manganese sesquioxide, inferior in oxidizing power to the binoxide. In steel and pig iron the error is practically inconsiderable, but with material like spiegel-eisen and ferro-manganese it may reach to one per cent or more of the manganese and cannot be neglected. It is always best to run a parallel determination on a sample of similar material in which the manganese has been determined gravimetrically, and make a correction therefrom.

5. Chatard's method. When a weak solution of manganous nitrate is acidified by nitric acid and boiled with lead peroxide or bismuth tetroxide, all the manganese is perduced to permanganic acid —

$$2Mn(NO_3)_2 + 5PbO_2 + 6HNO_3 = H_2Mn_2O_8 + 5Pb(NO_3)_2 + 2H_2O.$$

The excess of lead binoxide is removed by filtration through asbestos (paper would decompose the permanganic acid), and the solution titrated until colorless by a weak standard solution of any suitable reducing agent, such as oxalic acid, hydrogen peroxide, ferrous sulfate, mercurous nitrate, etc. Babbitt § prefers sodium arsenite —

$$5Na_3AsO_3 + H_2Mn_2O_8 + 19HNO_3 = 5H_3AsO_4 + 2Mn(NO_3)_2 + 15NaNO_3 + 3H_2O.$$

6. In the method of Moore the manganese is converted to sesquichloride and determined by titrating to protochloride by a ferrous solution, or from a reverse titration by ferrous sulfate and permanganate. The solution of iron

* Journ. Amer. Chem. Socy. 1893—113.
† Trans. A. I. M. E. 10—201.
‡ Trans. Amer. Inst. Mining Engrs. 11—323 etc.
§ Amer. Chem. Journ. 9—58.

and manganese is evaporated nearly to dryness and from ten to twenty Cc. of syrupy phosphoric acid added, then a few crystals of potassium chlorate, and the liquid warmed until the smell of chlorine has gone. The sesquioxide remains in solution coloring it a deep violet.

Colorimetric methods.* One of these, formerly much in use in steel works laboratories, is based on the measurement of the intense red color of permanganic acid. The reaction producing the acid is given in (5) *supra*. A decigram of steel is dissolved in a large test-tube in 20 Cc. of dilute nitric acid; the solution is heated and a few grams of lead peroxide added, and after boiling for a few minutes the excess of reagent is allowed to settle, leaving a clear supernatant solution of permanganic acid. An equal weight of another steel whose content of manganese is known is treated in the same way; the two liquids are decanted into graduated tubes of the same diameter, and the darker of the solutions is diluted with water until the tints are identical. Then the percentages of manganese are in proportion to the volumes of the two solutions.

Phosphorus. This element is believed to exist in steel and pig iron wholly or at least mainly, as an iron or manganese phosphide, possibly as iron titanum phosphide, while in wrought iron there is reason to suppose that part is in the intermingled slag as ferrous or manganous phosphate. Recent researches indicate that phosphorus, like carbon, may be in two forms or combinations, the proportions varying to some extent with the temperature of quenching the steel; they are differentiated by their unequal solubility when the steel is treated with a slightly acid solution of mercuric chloride.

Phosphorus, unlike sulfur, cannot well be determined by evolution as a hydrogen compound, so that invariably the analysis is begun by dissolving the metal in an oxidizing reagent, usually nitric acid of the specific gravity of 1.2 or 1.13; less often in aqua regia. With nitric acid of 1.2 the silicon of the metal is oxidized to silicic acid and dissolves, but on standing or when the phosphoric acid is precipitated, the silica partially separates; while with acid of 1.13 the silica remains in solution.

But whatever the strength of acid a phenomenon is observed, namely that instead of the whole, only a part (about two-thirds) of the phosphorus is oxidized to a compound precipitable by the usual precipitants for phosphoric acid; nor is the remainder converted thereto by boiling or evaporation of the solution to dryness, but only by heating the residue from evaporation up to about 120°,† or by boiling the original solution with some strong oxidizer such as potassium permanganate or chromic acid. This peculiarity was formerly attributed to the presence of silicone, later to carbon compounds; it occurs, however, to about an equal extent in pig iron and comparatively pure soft steel. Possibly some lower oxide of phosphorus is formed and restrained from passing to orthophosphoric acid by the associates; possibly meta- or pyro-phosphoric modifications may be the explanation. This characteristic has led some writers to erroneously depreciate the delicacy of the reaction between molybdic acid, ammonia and phosphoric acid in presence of much ferric nitrate.

Having the metal in solution and the phosphorus completely oxidized by heating the residue from evaporation or otherwise, first the phosphoric acid is

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* Trans. Amer. Inst. Min. Engrs. 51—102 and Journ. Anal. Chem. 1887—88 and 176. Age of Steel, 1901—23.

† Trans. Amer. Inst. Min. Engrs. 12—518.

to be separated from the iron and manganese, then precipitated in a combination suitable for weighing.

A. The "acetate-magnesia" method. The principles are these. (1) On boiling a nearly neutral solution of ferric acetate the compound is decomposed, all the iron precipitating as basic ferric acetate, and the precipitate carries down with it as ferric phosphate all the phosphoric acid that may be in solution if not too great in amount. Ferrous and manganous acetates are not decomposed by boiling their solutions. (2) From a solution of ferric chloride and phosphoric acid ammonia precipitates ferric hydrate and phosphate, but if certain organic bodies are also present, no precipitation takes place. (3) "Magnesia mixture" (an ammoniacal solution of magnesium ammonium chloride) precipitates phosphoric acid as magnesium ammonium phosphate, which on ignition loses ammonia, becoming magnesium pyrophosphate.

The nitric acid solution of the metal is evaporated to dryness, heated to 120°, dissolved in hydrochloric acid, and filtered from the silica and graphite. It is said that pyrophosphoric acid is formed on heating, but however this may be, it is reverted to the ortho-modification on dissolving the residue in hydrochloric acid. *Nearly* all the ferric chloride is reduced to ferrous chloride by sulfurous acid, sodium acetate added, and the solution nearly neutralized, boiled, and filtered. The small precipitate consisting of basic ferric acetate and ferric phosphate is dissolved in hydrochloric acid and a crystal of citric or tartaric acid. An excess of ammonia is added and the clear solution precipitated by magnesia mixture. The precipitate of ammonium magnesium phosphate is filtered off, washed by dilute ammonia, ignited, and weighed.

Instead of igniting the precipitate it may be determined volumetrically by finally washing with water, dissolving in excess of weak standard hydrochloric acid, and titrating back by standard ammonia. Malot * would dissolve it in nitric acid of 1.2 gravity and titrate by standard uranium nitrate; instead of the usual mode of determining the end-point by spotting with ferrocyanide, he prefers to mix with the titrate some extract of cochineal which forms a green precipitate (a lake) with uranium nitrate.

B. The "molybdate-magnesia" method. For general work this is probably the most reliable, and for any given class of material, quite as accurate as any method. The separation of the phosphoric acid from the iron and manganese is by the characteristic reaction of the acid with a colloidal solution of molybdenum trioxide in presence of ammonium nitrate, the formation of a canary granular precipitate of ammonium phospho-molybdate. The precipitate is almost, practically quite, insoluble in nitric acid in presence of molybdic acid, and in very dilute acids and solutions of their salts; but is readily decomposed by alkalies, the products passing into solution. Authorities differ as to the exact formula of the precipitate; it approximates $(NH_4)_3PO_4.11MoO_3.6H_2O$.

The metal is dissolved in dilute nitric acid, the solution evaporated to dryness and the residue heated to 120° or higher. The residue is then heated with concentrated hydrochloric acid and diluted with water, when all should go into solution except silica and graphite. After filtering, the solution is evaporated to dryness and the residue heated with concentrated nitric acid and diluted with water. There is now in solution ferric and manganous nitrates and phosphoric acid; the free nitric acid is nearly neutralized by ammonia, and the phosphoric acid precipitated by a large excess of a solution of molybdic acid in ammonium nitrate and nitric acid, and the mixture digested for several

* Chem. News, 1892—1—52.

hours, or what amounts to the same, vigorously stirred for ten minutes or more. The precipitate is filtered, washed with dilute molybdic solution or acidulated water, and dissolved in dilute ammonia.

A little alumina, ferric oxide or silica is usually carried down with the yellow precipitate. To remove them, the solution is neutralized by hydrochloric acid, heated and filtered. The small precipitate retains traces of phosphoric acid which can be recovered by dissolving the precipitate in dilute nitric acid and precipitating by molybdic solution. A simpler plan is to add a small crystal of citric acid to the ammoniacal solution, the ammonium citrate preventing their precipitating with the magnesium ammonium phosphate.

Modifications of the above are in the use of nitric acid of a gravity of about 1.13, and the oxidation of all the phosphorus by potassium permanganate or other oxidizer. This avoids the necessity of evaporation, as the silica remains in solution in the acid and does not interfere with the precipitation of the phosphoric acid.

Molybdic acid is freely soluble in dilute ammonia and so the precipitate of ammonium magnesium phosphate should retain none of it. But ammonium compounds of other oxides of molybdenum than the trioxide are prone to be occluded, and to prevent or remove this contamination it has been recommended: (1) before precipitation to oxidize by bromine water the lower molybdenum oxides to the trioxide; (2) before precipitation to saturate the ammoniacal solution by hydrogen sulfide, then acidulate and filter off the precipitate of molybdenum sulfide; or (3) to strongly ignite the magnesium pyrophosphate to volatilize the molybdenum oxides.

C. Riley's method* proposes to unite the advantages of the acetate-magnesia and the molybdate-magnesia methods. He proceeds according to the former until there is obtained the small precipitate of basic ferric acetate containing the ferric phosphate, dissolves it in nitric acid, precipitates by molybdic solution, and continues according to the latter method. In reality the scheme includes the weakest points of both — the liability of incomplete precipitation of the phosphoric acid in the former, and in the latter the contamination of the magnesium precipitate by molybdenum oxides and the impurities of commercial molybdic acid.

D. The direct molybdate method. A scheme, formerly much in use, is that of obtaining the precipitate of ammonium phospho-molybdate of as definite a composition and as free from extraneous molybdic acid as possible, filtering on a tared paper or through two counterpoised filters or a Gooch crucible, washing with water or dilute alcohol, drying the precipitate at 100°, and weighing it. Under these conditions the precipitate is assumed to contain 1.63 per cent of its weight of phosphorus. To favor the formation of a precipitate of constant composition, Carnot would dissolve the washed precipitate in dilute ammonia, and reprecipitate under fixed conditions.

Modifications of the above are: (1) instead of taring the filter, the dried precipitate may be brushed out upon a tared watch-glass, the slight mechanical loss in this operation having less effect on the accuracy of the determination than would usually follow, on account of the small percentage of phosphorus in the precipitate; (2) the undried washed precipitate is dissolved through the filter in dilute ammonia, catching the solution in a tared basin, and evaporating to dryness on the water bath; (3) the precipitate may be moderately ignited to expel the ammonia and water and the residue weighed as $24MoO_3.P_2O_5$; (4) the precipitate may be suspended in water or other liquid and its weight

* Journ. Chem. Socy. 1878—104.

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determined by the increased specific gravity of the latter; (5) the ammonia in the precipitate may be determined by distilling the precipitate with an excess of sodium hydrate and Nesslerizing the distillate; the phosphorus and ammonia are said to bear a more constant correllation in the yellow precipitate than does the phosphorus to the molybdic acid.

For rapid approximate determinations in laboratories of steel works the Goetz modification * of Eggertz' method is in common use. A small standard weight of steel is dissolved in dilute nitric acid, the phosphorus oxidized by permanganate, and the manganic oxide dissolved as in Hundeshagen's method (*post*); the solution is transferred to a pear-shaped bulb, Fig. 3, with a graduated prolong of standard internal diameter. Molybdic solution is added and the bulb whirled in a centrifugal machine for a few minutes. The apparent volume of the precipitate, packed in the prolong, is read. As the prolong is of a uniform diameter the height of the column is proportional to the weight of the precipitate, and is graduated by the maker directly in tenths and hundredths of one per cent of phosphorus.

E. A number of other schemes for separating all or most of the iron and manganese from the phosphorus have been proposed, such as by dissolving the metal in a solution of ferric chloride or of copper ammonium chloride, the phosphorus remaining in the residue; precipitating the iron electrolytically, by a ferrocyanide, etc., but none have come into general use.

F. Volumetric methods. All these measure either the molybdic acid or the molybdic plus phosphoric acids in the yellow precipitate, and therefore depend for their accuracy upon the constancy of the composition of the precipitate. As this is conceded to be somewhat variable, either *per se* or by the co-precipitation or subsequent precipitation of molybdic acid, even when the conditions of the operation comply with fixed rules, volumetric methods should be restricted to material in which the percentage of phosphorus is approximately known, and where any considerable variation from the expected percentage can be checked by a gravimetric method. In their favor is the magnitude of the ratio between the molybdenum trioxide and the phosphorus of the precipitate — about 91.4 to 1.63, and the small percentage of phosphorus contained in merchantable iron and steel.

Emmerton's method.† A clear nitric solution of the metal is prepared as in the molybdate-magnesia method; all the iron is precipitated by ammonia, then, without filtering, redissolved in a limited excess of nitric acid. The solution is heated and precipitated by molybdic solution, with vigorous shaking. It is then filtered, and the yellow precipitate washed with a weak solution of ammonium nitrate or sulfate, and dissolved in dilute ammonia. The ammoniacal solution is strongly acidified by sulfuric acid and metallic zinc introduced; the nascent hydrogen evolved reduces the molybdic trioxide to a lower oxide or mixture of oxides, said to be $Mo_{12}O_{19}$ (Emmerton), or Mo_2O_3 (Cheever)

$$12MoO_3 + 17Zn + 17H_2SO_4 = Mo_{12}O_{19} + 17ZnSO_4 + 17H_2O; \text{ or}$$
$$2MoO_3 + 3Zn + 3H_2SO_4 = Mo_2O_3 + 3ZnSO_4 + 3H_2O.$$

When the reduction is complete, the solution becoming of a dark green color, the excess of zinc is withdrawn by filtration. In the filtrate the molybdenum suboxide is re-oxidized to the trioxide by titration by an empirical standard solution of potassium permanganate —

$$5Mo_{12}O_{19} + 17K_2Mn_2O_8 + 68H_2SO_4 = 60MoO_3 + 34KHSO_4 + 34MnSO_4 + 51H_2O; \text{ or}$$
$$6Mo_2O_3 + 3K_2Mn_2O_8 + 12H_2SO_4 = 10MoO_3 + 6KHSO_4 + 6MnSO_4 + 9H_2O.$$

* Zeits. angew. 1889—638.

† Trans. Amer. Inst. Mining Engrs. 15—96 and Compt. Rend. 59—301.

As the oxidization proceeds, the dark color of the liquid gradually lightens until colorless, and another drop of permanganate reddens it. All the operations are to be performed according to specified directions.

The molybdic acid may also be reduced by passing the solution through a Jones' "reductor," * Fig. 173. The tube A is filled with powdered zinc and the flask F connected to a filter pump. The solution is poured into the funnel B and is forced into F by the pressure of the air on the surface. After washing the zinc by dilute sulfuric acid and water (preventing the passage of air by keeping the tube full of liquid) the solution is ready for titration. The formula of the molybdenum suboxide formed is said to differ somewhat from that given above.

Fig. 173. 1/8

Hundeshagen's method, modified†. The steel is dissolved in dilute nitric acid and the phosphorus completely oxidized by boiling with potassium permanganate. The precipitated manganic oxide, coming from decomposition of permanganic acid, is reduced by heating with a few grains of sugar and passes into solution as nitrate, *e. g.*,

$$24MnO_2 + C_{12}H_{22}O_{11} + 48HNO_3 = 24Mn(NO_3)_2 + 12CO_2 + 35H_2O.$$

The yellow precipitate is thrown down by molybdic solution, the deposition hastened by brisk stirring or shaking, filtered, and washed with a neutral solution of potassium nitrate. It is then dissolved in an excess of weak standard sodium hydrate —

$$(NH_4)_3.11MoO_3.PO_4 + 25NaOH = 3NH_4OH + 11Na_2MoO_4 + Na_3PO_4 + 11H_2O;\ \text{or}$$
$$(NH_4)_6(PO_4)_2.(MoO_3)_{24} + 46NaOH = (2NH_4)_2HPO_4 + (NH_4)_2MoO_4 + 22H_2O + 23Na_2MoO_4.$$

The excess of alkali is then found by titration by weak standard nitric acid and phenol-phthalein. The alkali and acid are standardized against ammonium phosphomolybdate precipitated under the same conditions as obtain in the analysis.

A colorimetric method depends on the brown color developed when molybdic acid is reduced by stannous chloride. The yellow precipitate is dissolved in potassium hydrate solution, this boiled to expel ammonia, cooled and acidified by hydrochloric acid, and stannous chloride added. The color is compared with that of a standard solution of molybdic acid in hydrochloric acid. The same reaction is the basis of a volumetric method; the slight excess of stannous chloride is converted to stannic chloride by mercuric chloride, and the molybdous oxide titrated by bichromate of potassium.

Sulfur. With respect to the nature and concentration of the reagent chosen to dissolve the iron or steel, the sulfur may: (1) pass into solution as sulfuric acid or a soluble sulfate; (2) remain in the insoluble residue as iron or manganese sulfide or as free sulfur; or (3) be converted to gaseous hydrogen sulfide.

1. The 'aqua regia' method. The metal in thin shavings or fine powder is treated with concentrated nitric acid; prolonged boiling is required for solution since

* Trans. Amer. Inst. Mining Engrs. 15—625.

† Journ. Anal. Appl. Chem. 1892—82 and 204; *Idem*, 6—242.

the metal becomes passive when immersed in the cold concentrated acid. To the solution is added a little potassium nitrate to form potassium sulfate (ferric sulfate is decomposed on heating), evaporated to dryness, and heated for some time to 110° to render silica insoluble. The residue is dissolved in hydrochloric acid, filtered from silica and graphite, largely diluted, and the sulfuric acid precipitated by barium chloride. The method is fairly accurate, the plus error from contamination of the barium sulfate by iron oxides, silica, etc., being compensated to a degree by the solubility of the precipitate in acid ferric chloride. The weighed precipitate may be purified by boiling with concentrated hydrochloric acid, diluting with water, adding a little barium chloride, then filtering and weighing as before; the more usual method, inaugurated by a fusion with sodium carbonate, may easily introduce more impurities than are extracted.

Other solvents for the metal are aqua regia which dissolves the iron promptly, but there is said to be some danger of loss of sulfur by volatilization of sulfur chloride; bromine in hydrochloric acid; potassium bromide or potassium chlorate with nitric acid; etc.*

The injurious effect of the ferric chloride to dissolve barium sulfate or contaminate it is avoided by precipitating the iron by ammonia, and determining the sulfuric acid in the concentrated filtrate.

2. The metal is treated with some solvent which has neither an oxidizing action nor generates hydrogen with the iron or manganese. In this class are nearly neutral ferric chloride —

$$Fe + Fe_2Cl_6 = 3FeCl_2, \text{ and } Mn + Fe_2Cl_6 = MnCl_2 + 2FeCl_2 —$$

copper ammonium chloride, etc. All these leave the sulfur in the residue, from which it may be dissolved by concentrated nitric acid and the solution treated as in (1). The precipitation taking place in a solution almost free from ferric chloride, there is no loss from solubility and the precipitate is pure.

3. In "evolution methods" the sample is dissolved in dilute hydrochloric acid, and the hydrogen evolved, carrying the hydrogen sulfide, is passed through an absorbing medium. For a gravimetric determination the absorbent is (1), a solution of an oxidizer, such as potassium permanganate, bromine in hydrochloric acid, or hydrogen peroxide in ammonia, these converting the hydrogen sulfide into sulfuric acid to be precipitated by barium chloride and weighed as barium sulfate; or (2), a solution of some metallic salt, as an ammoniacal solution of silver nitrate, lead acetate, or cadmium chloride; in these a sulfide of the metal is precipitated, the precipitate filtered off, washed, dried and weighed as such, or oxidized by nitric acid to the sulfate, and the sulfuric acid determined in the usual way.

One of the many forms of apparatus is shown in Fig. 73. The weighed drillings are placed in the flask A, and the funnel tube B is filled with dilute acid. The absorption bulb C holds the oxidizing or absorbing reagent. The acid in B is run into A, and when the metal has dissolved, the solution is heated to boiling to expel what hydrogen sulfide remains dissolved and in the gas in the flask. At the same time a stream of air may be forced through the apparatus entering at B, by pressure or by suction at D. In more accurate analyses, the air in the flask and bulbs, that might oxidize some of the hydrogen sulfide to sulfurous acid, is displaced by a stream of hydrogen or carbon dioxide before running in the hydrochloric acid. As a further precaution, Campredon † would pass the gases through a red-hot

* Journ. Amer. Chem. Socy. 1901—675.

† Chem. News, 1895—2—15.

porcelain tube preceding the absorption bulb, the hydrogen reducing any sulfurous compounds to hydrogen sulfide.

A quick volumetric method, much in use at steel works, is that of passing the evolved gases through a strong solution of potassium hydrate or sodium hydrate, the hydrogen sulfide reacting to form alkali sulfide. The caustic solution is largely diluted, then acidified by hydrochloric acid, this setting free hydrogen sulfide which remains dissolved in the bulky cold liquid. The solution is immediately titrated by a standard solution of iodine, using starch-paste for an indicator.

Owing to the absorption of hydrocarbons by the alkali solution, the standardizing of the iodine solution is best done by a parallel determination on a similar grade of metal whose content of sulfur has been ascertained by a gravimetric determination.

Boucher* modifies the above by absorbing the hydrogen sulfide in dilute caustic soda solution, pouring this into a strongly acidified solution of ferric chloride, and titrating the ferrous chloride (reduced from ferric by the hydrogen sulfide), by weak standard potassium bichromate.

For the caustic alkali solution may be substituted an ammoniacal solution of cadmium sulfate or zinc sulfate. After filtering, the precipitated sulfide is dissolved in dilute acid and titrated. An advantage of this plan is that the interfering effect of the hydrocarbons absorbed by the alkali is to a great extent eliminated.

An approximate technical method is described by Arnold and Hardy. The gases from the evolution flask are passed through a series of some fifteen small absorption tubes, each containing exactly two cubic centimeters of a solution of lead acetate of a fixed concentration. The strength of the lead solution is such that each absorption tube contains the exact amount of lead precipitable by the hydrogen sulfide corresponding to .01 per cent of sulfur in the standard weight of metal dissolved. When the gas has passed, the number of bulbs showing a precipitate or coloration represents the number of hundredths of one per cent of sulfur in the steel. No hydrogen sulfide is retained in solution by the liquid in any bulb on account of the large volume of hydrogen accompanying it.

The results of all determinations are likely to be somewhat too low, especially for pig iron or cast iron, as some of the sulfur remains with the insoluble matter in the flask, perhaps as an organic compound or as ferrous disulfide. Blair† observed in a sample of pig iron containing titanium and vanadium, that the major part of the sulfur was in a form of combination insoluble in either hydrochloric, nitric, or nitro-hydrochloric acids, and was only to be resolved by fluxing. According to Moore the condition of the carbon in cast iron exerts an influence on the amount of sulfur retained in the insoluble residue, a greater proportion remaining in the case of chilled iron than in the same iron that has slowly cooled from a fused condition.

In all accurate analyses, therefore, the insoluble residue is filtered from the solution of ferrous chloride, treated with nitric acid, evaporated to dryness, taken up by hydrochloric acid, filtered, and the filtrate tested by barium chloride; if a weighable amount of barium sulfate forms it is determined as usual. The solution of the ferrous chloride may also be tested by barium chloride, though it seldom if ever contains sulfur.

4. Phillips‡ calls attention to the readiness with which finely powdered iron

* Chem. News, 1897—121.

† Journ. Amer. Chem. Socy. 1897—114.

‡ *Idem*, 1897—1079.

is oxidized by a melted mixture of sodium carbonate and nitrate, and the simultaneous complete oxidation of all the sulfur to sulfuric acid. Bamberg recommends a modification of the aqua regia method, wherein the solution of the metal in concentrated nitric acid is evaporated with sodium nitrate in a platinum dish and the residue ignited. During the ignition the sulfur is exposed to the intense oxidizing action of the melted sodium nitrate and the decomposing ferric nitrate. The melt is lixiviated by a solution of sodium carbonate, acidulated, evaporated to separate silica, the residue taken up by dilute hydrochloric acid, filtered, and the sulfuric acid precipitated by barium chloride.

5. Eggertz many years ago proposed a colorimetric scheme for wrought iron and steel, in which a decigram of the metal is dissolved in dilute sulfuric acid in a small flask, the hydrogen sulfide evolved impinging on a polished silver plate. A tarnish of silver sulfide ensues, the depth of the tint being in proportion to the percentage of sulfur in the metal, ranging from light yellow (.01 per cent) to brown (.04 per cent). For comparison, irons containing known amounts of sulfur are treated in the same way. The results are only approximate at best, and the method is but little used. Later the principle was revived by Wiborgh * who passes the gas through a disk of white cotton cloth mordanted with a standard solution of cadmium acetate; a yellow coating of cadmium sulfide is produced, deep in proportion to the hydrogen sulfide transpiring.

Carbon. Since no practical methods for the proximate analysis of iron and steel have as yet been devised, a discussion of the question as to the condition or form of combination in which carbon exists in the metals need not be entered into. Two conditions are readily differentiated, however: (A), *combined* (or *dissolved*) carbon, by its behavior when the metal is dissolved (1) in a non-oxidizing acid, the carbon passing off as a mixture of gaseous hydrocarbons; (2), in hot dilute nitric acid, the carbon slowly entering into solution as a hydrated, highly tinctorial compound; and (3), in a solvent of a reducible nature, leaving the carbon as a soft, black, pulverulent residue insoluble in dilute acids, probably a carbohydrate (C_3H_2O ?), that dries to a fine powder burning like tinder when heated in oxygen or air. (B), Carbon in the graphitoidal form (shortly *graphite*), practically unaffected by acids and exhibiting the physical characteristics of the mineral — slow combustibility, an unctuous feel, etc. There is also a third form, a psuedo-graphite, whose properties are intermediate between the other two. The carbon in steel is assumed to be entirely in the combined state except in metals of some unusual chemical composition or that have been subjected to abnormal physical treatment.

Outside of comparative methods, the general procedure in a determination is to convert the carbon into carbon dioxide and, by weighing or otherwise, find the proportion of carbon contained. A great number of methods have been devised, nearly all for the estimation of the total carbon of the metal.

1. The carbon is oxidized to carbon dioxide simultaneously with the oxidation of the iron and manganese.

A. The metal is heated in a current of oxygen, either alone or mixed with a reagent readily parting with oxygen. It is essential that it be in the form of the thinnest shavings or as a fine powder, that the coating of sintered magnetic oxide or sesquioxide of iron may not protect the interior from oxidization.

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* Journ. Socy. Chem. Ind. 9—16.

The metal is spread over the bottom of a capacious porcelain or platinum boat, then heated to bright redness in a porcelain or platinum combustion tube arranged as for an ultimate organic analysis. The success of the operation is more certain if a greater weight of some carbon-free oxidizer like copper oxide, lead dichromate or potassium chlorate is intermixed with the metal.

B. The metal is dissolved directly in a hot concentrated solution of chromic acid in moderately dilute sulfuric acid. The iron and manganese dissolve as ferric and manganous sulfates, while the carbon is oxidized to carbon dioxide by the combined action of chromic acid and ferric sulfate; above a certain concentration of the reagent, oxygen also is produced — $2CrO_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 3O + 3H_2O$. For graphitic irons it is a safer plan to pass the gases through a porcelain tube filled with copper oxide kept at a red heat, in order to oxidize any carbon monoxide or hydrocarbons of the gas.

2. The iron and manganese are separated from the carbon, and the carbonaceous residue submitted to analysis.

A. The metals are volatilized by heating in a current of dry, oxygen-free chlorine. The metal is weighed in a porcelain boat and the boat pushed to the middle of a combustion tube, whose anterior end is sealed by a water-trap. The ferric chloride formed on heating sublimes to anhydrous yellow flakes. When all the metal has been carried over, the tube is cooled and the boat transferred to an apparatus for ultimate organic analysis.

B. When iron or steel is dissolved in dilute hydrochloric acid under the influence of an electric current of suitable density, the chlorine liberated by the electrolysis of the acid unites with the iron to form ferrous chloride, and the hydrogen escapes at the negative pole. As no hydrogen is evolved at the surface of the iron, the carbon does not pass off as hydrocarbons, but remains in the solid form, retaining the shape of the original fragments of the metal.

The metal drillings are held in a basket of platinum gauze which hangs in the acid and is connected to the copper pole of a battery; to the zinc pole is connected a piece of platinum foil hung some distance from the basket. The current is known to be properly adjusted when the stream of the heavy solution of ferrous chloride falling from the basket is colorless.

C. Bromine in aqueous solution, and iodine in a solution of potassium iodide unite directly with iron and manganese to form their bromides or iodides, and since no hydrogen is evolved, leave the carbon as a residue. It is essential that the solvent be at or below the ordinary temperature while the metal is undergoing solution since the carbon has a rather high chemical potential at the instant of liberation, and a soluble compound with the halogen may occur to some extent at higher temperatures.

D. Solutions of various metallic salts that are reduced to a lower state of oxidation, or from which the whole or part of the base may be displaced by iron or manganese, have been proposed; such are cupric, mercuric, and ferric chlorides in aqueous solution, and silver chloride in the solid form. Thus, a slightly acid solution of ferric chloride dissolves an atom of iron by parting with two atoms of chlorine; and a cold solution of potassium dichromate in dilute sulfuric acid dissolves the metal without evolution of hydrogen —

$$K_2Cr_2O_7 + 3H_2SO_4 + Fe_2 = Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + 2KHSO_4 + 7H_2O.$$

Both cupric sulfate and chloride deposit an equivalent of copper for the iron, taken up if desired, by heating with dilute hydrochloric acid or ferric chloride in which the carbon residue is insoluble. A mixture of cupric and ferric chlorides has been advised, the latter compound reacting with the cuprous chloride as soon as produced, the products being cupric and ferrous chlorides.

Lunge asserts that there is a loss of carbon during solution in cupric salts

from the formation of gaseous carbon compounds, amounting to .027 per cent with cupric sulfate as a solvent, and to .015 per cent with copper ammonium chloride. To recover the carbon in the gases he would dissolve the metal under a slow current of pure air; from the dissolving vessel the air passes over hot copper oxide to burn the carbon gases to carbon dioxide, thence through potash bulbs to absorb the latter and allow its being weighed.

The double chloride of an alkali metal and copper dissolves iron without the deposition of copper — $Fe + 2CuCl_2(KCl)_2 = FeCl_2 + Cu_2Cl_2(KCl)_4$; or taking the formula Fe_3C to represent the normal combination of carbon and iron, $3\,Fe_3C + 18CuCl_2(KCl)_2 + H_2O = 9FeCl_2 + 9Cu_2Cl_2(KCl)_4 + C_3H_2O(?)$. A strongly acidulated solution of a double chloride has been found to yield higher results for carbon than a neutral solution. It may be that the latter fails to decompose all the iron carbide or some one variety of this compound, afterward dissolved, with evolution of hydrogen and loss of carbon, on washing the residue with dilute hydrochloric acid.

The carbon left after extraction of the iron and manganese by one of the methods given above cannot well be dried and weighed directly since it is combined with hydrogen and oxygen, perhaps in indefinite proportions, or contains graphite, and is often mixed with silica, scale or sand coming from the metal drillings and insoluble in dilute acid. Therefore the carbon contained is best determined by the usual process for the determination of carbon in an organic compound. The liquid is filtered on purified asbestos and the residue washed with dilute hydrochloric acid and water.

For the oxidation of the carbon and the determination of the carbon dioxide produced, one has a choice of several methods. The dried residue may be mixed with powdered cupric oxide and burned in a current of air; burned alone in air or oxygen; or, without drying, transferred to a flask and oxidized by chromic and sulfuric acids. The carbon dioxide formed is passed through a drying tube, thence through a potash bulb.

Shimer* has arranged a special apparatus for the combustion, a substitute for the platinum combustion tube. As shown in section in Fig. 174, a platinum crucible is closed by a hollow metal stopper A, through which circulates cold water, and the junction made gas-tight by a rubber band. Around the upper part of the crucible is a water-cooled ring B, to prevent the rubber gasket from being heated. Passing through the stopper are inlet and outlet tubes C and D, for the gases.

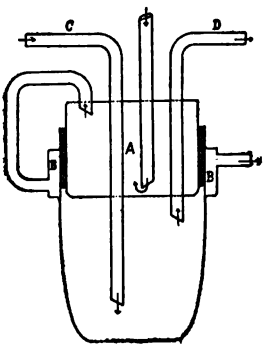

Fig. 174.

Combined carbon. This is usually found by difference, subtracting the result for the graphite from that for the total carbon. Two methods have been proposed for a direct determination.

A. The metal is dissolved in dilute sulfuric acid and the hydrogen, hydrocarbons, and hydrogen sulfide passed through a porcelain tube containing red-hot copper oxide; the hydrogen burns to water, the carbon to carbon dioxide, and the sulfur to sulfuric acid. The carbon dioxide is collected and weighed as in an elementary analysis.

B. The metal is dissolved in melted potassium pyrosulfate, sulfurous and carbonic acid gases being evolved. The mixed gases are passed through chromic acid to oxidize and absorb the sulfurous acid, then over hot copper oxide

* Journ. Amer. Chem. Socy. 1901—227.

to burn any carbon monoxide or hydrocarbons in the gases, finally into a potash-bulb. The graphite of the metal is said to be unattacked and may subsequently be determined after lixiviating the flux with water.

Graphite. It is generally assumed that in steel, wrought iron, spiegel-eisen and ferro-manganese all the carbon is combined or dissolved in the metal, but graphitic carbon is also present in pig iron, cast iron, malleable castings, and some spiegels. The graphite is determined by dissolving the sample in a dilute acid, boiling, filtering and washing with dilute potassium or ammonium hydrate and water — some recommend also alcohol and ether — to remove any adhering hydrocarbons, and making a combustion of the residue as above described. Or the residue may be dried and weighed, then burned in a platinum crucible and the weight of the remaining silica, etc., deducted. In any case, the results are open to criticism, as with hydrochloric or sulfuric acid for the solvent, part of the combined carbon may separate in a form insoluble in the washing fluids, and with nitric acid, the finely divided carbon may not entirely escape oxidation. Titanium carbide, a common constituent of pig iron, is insoluble in hydrochloric acid, but readily decomposed by nitric.

Colorimetric method for combined carbon. Eggertz† in the year 1862, observed that when pure iron is dissolved in hot moderately dilute nitric acid the solution is practically colorless after moderate dilution with water, while in the case of a steel, the carbon, at first separating in flocks, slowly dissolves and colors the acid brown or greenish-brown, the intensity of the tint varying directly with the proportion of carbon in the steel. On this principle he contrived the method now in general use. A standard weight (.1 to 1 gram) of drillings is dissolved in a test-tube in a standard volume (8 to 15 Cc.) of nitric acid of about 1.2 specific gravity. The solution is heated in the water-bath for ten to thirty minutes, then diluted, cooled, and filtered if necessary, and poured into a comparison tube graduated in cubic centimeters. A 'standard' steel (one whose carbon has been determined gravimetrically) is treated at the same time in exactly the same manner. The darker of the solutions is then diluted until the tints are the same, when the percentages of carbon in the standard and sample are directly as the volumes of the respective solutions.

A rack of hermetically-sealed tubes (Fig. 144) containing solutions of steels of different percentages of carbon may be prepared, but their colors are not permanent, fading on exposure to light. This objection applies, though in a less degree, to such substitutes as tinctures of roasted coffee, caramel, etc., and solutions of ferric salts tinged with copper and cobalt.

The condition or form of combination of carbon, consequent on the mode of manufacture or subsequent mechanical or heat treatment of the steel, determines to a certain extent the depth of tint, so that the steel selected for a standard must have been manufactured by the same process and have received approximately the same after-treatment as the sample to be compared with it.† Following the general rules for colorimetric determinations, the solutions to be compared must be clear (free from suspended sulfur, scale, etc.) and of about the same concentration, that is, the standard is to be of approximately the same percentage of carbon as the sample to be tested. Observing these precautions, the method in practiced hands is remarkably accurate for one of its class.

The nitric acid solutions of the softer steels are apt to differ in color as well as tint, making a comparison difficult. Stead directs to precipitate the iron as ferric hydrate by solution of sodium hydrate in excess; the colorific carbon com-

* Trans. Amer. Inst. Mining Engrs. 12—303.
† Chem. News, 1894—1—251.

pounds are left in solution, their tints intensified but their colors identical. After diluting the solutions to a definite volume and filtering, aliquot portions of the filtrate are compared in the usual way. He has devised a special colormeter for matching the faint shades.

Copper. All or nearly all of this element remains in the insoluble residue when the metal is dissolved in dilute sulfuric acid. After saturating the solution with hydrogen sulfide, or boiling with a little sodium thiosulfate to precipitate any traces of copper that may have gone into solution, the liquid is filtered; the residue is treated with nitric acid, evaporated to dryness, taken up with hydrochloric acid, and filtered from silica and graphite. From the filtrate the copper is precipitated as sulfide, roasted to cupric oxide and weighed; or the filtrate is evaporated with sulfuric acid and the copper deposited electrolytically.

Arsenic. On dissolving steel in dilute hydrochloric acid the arsenic present does not escape as arsine but remains in solution as arsenic chloride, and on dilution and treatment with hydrogen sulfide, precipitates as arsenious sulfide. The steel is dissolved in dilute hydrochloric acid, and treated with a little sulfurous acid, then warmed until the sulfurous acid is dissipated. A stream of hydrogen sulfide precipitates the sulfide; the solution is filtered and the precipitate digested with potassium sulfide which dissolves the arsenic but leaves the copper and iron sulfides. The solution is filtered and the filtrate acidified, reprecipitating the arsenic as sulfide. Again filtering, the precipitate is oxidized to arsenic acid by hydrochloric acid and potassium chlorate. The solution is made ammoniacal and precipitated by magnesia mixture, the arsenic coming down as ammonium magnesium arseniate. This compound, analogous to the corresponding phosphate, leaves magnesium pyroarsenate on ignition.

In another method, the arsenic is converted into arsenic acid by nitric acid; on heating with hydrochloric acid and a strong reducer, the arsenic passes to arsenic chloride that may be distilled at the boiling point of strong hydrochloric acid. The steel is dissolved in a mixture of nitric and sulfuric acids and evaporated until all nitric acid is expelled and the residue forms a dry cake. This is transferred to a flask, powdered ferrous sulfate and strong hydrochloric acid added, and the mixture distilled into cold water. In the distillate the arsenic is determined by precipitating by hydrogen sulfide and pursuing the usual course for a determination.

Iron. In analyses of commercial iron and steel the iron is usually determined by difference, and frequently also in spiegels and ferromanganese in which the percentage of iron is secondarily important to that of manganese. A fair approximation to the percentage of iron in the two manganiferous metals can be had by determining the manganese, deducting a certain percentage for carbon, silicon, etc., and calling the remainder iron. The percentage deducted for the carbon, silicon, etc., varies with the manganese content of the metal but is quite constant for a given percentage.

A direct determination is made by a process similar to that used for the deter-

mination of iron and iron ores. The metal is dissolved in dilute sulfuric acid and the ferrous sulfate titrated by potassium permanganate, or in hydrochloric acid and the ferrous chloride titrated by potassium bichromate. Usually the carbon must be eliminated, since dissolved hydrocarbons reduce permanganate and to a less extent, bichromate; this can be accomplished by heating the solution to boiling, filtering, and treating the filtrate with potassium chlorate. The liquid is then reduced by zinc or other reagent and titrated as usual.

Of commercial iron and steel, carbon, silicon, sulfur, phosphorus, and manganese are invariable constituents, and as their effect on the quality of these metals has been studied and approximate limits established for the different varieties, they are always included in an analysis. Copper and arsenic are not infrequently found, and titanium, tin, zinc, nickel and a few other elements more rarely, although minute traces of many unsuspected elementary constituents would probably be found by a careful search. For the methods of determining the elements not described here, reference may be had to several practical works on iron and steel analysis that have been published by Troilius, Blair, von Jonsdorff, and Arnold.

Besides the familiar carbon-hardened steel there are on the market a number of special alloys of remarkable physical properties, known from the influential adjective as tungsten- manganese- chrome- nickel- silicon- titanium- and aluminum-steel, some of these having attained considerable practical importance. For the production of such steels there are manufactured alloys of iron with a high percentage of these elements, designated as ferro-chrome, ferro-tungsten, silico-spiegel, etc. The methods for the determination of these elements follow in the main those well known and of general application.

IRON AND MANGANESE ORES.

The minerals constituting the ores of iron are either hematite (Fe_2O_3), limonite ($Fe_2O_3.xH_2O$), magnetite (Fe_3O_4), or siderite ($FeCO_3$). The common associates are oxides of manganese, quartz, various hydrous and anhydrous silicates of the earths and alkalies, etc., and small percentages of phosphoric acid compounds, and sulfur in the form of pyrite or gypsum. Frequently also are found bituminous matter and titanic acid, more rarely the oxides or other compounds of arsenic, copper, zinc, nickel, chromium, etc. All ores contain hygroscopic moisture in variable quantity.

The commercial value of an ore is based primarily on the content of iron and manganese, and freedom from titanic acid, phosphoric acid and sulfur. It is also a desideratum that the gangue contain a considerable proportion of lime or magnesia rather than be wholly or mainly silica or aluminum silicates. A 'Bessemer ore' is one suitable for the manufacture of rail-steel by the acid Bessemer process; that is, that the resulting steel shall not contain over about one-tenth of one per cent of either phosphorus or sulfur. Where charcoal is the fuel used in the blast furnace the limits of phosphorus and sulfur in a Bessemer ore may be taken as not to exceed a ratio of .07 per cent to 65 per cent of iron in the ore; with coke fuel, the sulfur in the ore must be lower.

Manganese ores, from which are smelted spiegel-eisen and ferro-manganese, are essentially one or a mixture of the hydrated or anhydrous higher oxides of manganese, and usually contain associated ferric oxide or hydrated oxide. They are valued, next to the content of manganese and iron, by their freedom from silica. Phosphorus is nearly always comparatively high in these ores, and baryta is a frequent associate.

Below are a few analyses of different varieties of ores, all dried at 100° previous to analysis.

	A.	B.	C.	D.	E.
Ferrous oxide	1.22	24.49	45.27	.36	.....
Ferric oxide	87.67	68.22	.64	72.28	4.37
Silica	5.21	2.99	11.24	12.76	10.96
Alumina	2.07	1.07	8.14	.31	1.73
Lime	.93	.65	1.72	.42	6.77
Magnesia	.56	.20	1.51	.17	.66
Manganese oxide	.30	1.21	.....	2.83	67.60 (Mn_3O_4)
Phosphoric acid	.14	.07	.17	.54	.21
Sulfur	.03	2.11	trace	.10	.08
Carbon dioxide	.....	.....	30.32	.....	.....
Titanic acid	.....	3.20	.....	.....	.....
Organic matter, Combined water	1.48	.28	.98	10.40	6.33
Baryta	.....	.....	.....	.....	.37
	99.61	99.49	99.99	100 17	99.08
Metallic iron	63.32	63.51	35.66	50.91	3.06
Phosphorus	.061	.035	.074	.237	.092
Manganese	.19	.76	.....	2.19	48.71

A, Lake Superior hematite. B, New York magnetite. C, Pennsylvania siderite. D, Tennessee limonite. E, Chilian pyrolusite.

Most iron ores dissolve but slowly and with difficulty in sulfuric acid anare practically insoluble in nitric acid, so that hydrochloric is the invariable solvent. If it is desirable for any given determination that the bases be combined as sulfates or nitrates, the hydrochloric solution is evaporated with an excess of sulfuric, or boiled down two or three times with nitric. A few ores are so dense in structure as to be but slowly acted on by concentrated hydrochloric acid; here a previous ignition in hydrogen will reduce the oxide to metal, or the addition of a reducing agent to the hydrochloric acid, if allowable, will hasten the operation.

Iron. This, the most important constituent of an iron ore, is always determined volumetrically since gravimetric methods are far more laborious and not more accurate. The volumetric methods depend on the conversion of a ferrous compound to a ferric compound by a perducer, usually potassium permanganate or bichromate; less frequently the conversion of a ferric to a ferrous compound by a reducing agent.

A. By standard permanganate. All the iron is brought to the state of ferrous sulfate in a dilute sulfuric acid solution, and titrated by standard potassium permanganate. A gram of the dried ore is dissolved in hydrochloric acid, diluted and filtered; if any iron is contained in the insoluble residue, it is brought into solution, easiest by heating the residue contained in a platinum dish, with hydrofluoric and sulfuric acids, evaporating to remove the hydrofluosilicic and excess of hydrofluoric acids, dissolving the residue in hydrochloric acid, and adding the solution to the main solution. An excess of sulfuric acid is added and the liquid evaporated until all hydrochloric acid is expelled, then diluted with water. The ferric sulfate in solution is reduced to ferrous sulfate by metallic zinc, then decanted from the excess of zinc, and at once titrated. The accuracy of the result is vitiated only by carbonaceous matter in quantity too great to be destroyed by the evaporation with sulfuric acid, and which should have been eliminated by roasting the ore previous to dissolving it; and by titanic acid *q. v.* The reaction of the titration is

$$10FeSO_4 + K_2Mn_2O_8 + 9H_2SO_4 = 5Fe_2(SO_4)_3 + 2KHSO_4 + 2MnSO_4 + 8H_2O.$$

Although proceeding in this manner gives satisfactory results, the time required for evaporation and the slow reduction by zinc are serious drawbacks in technical work. A hydrochloric solution of iron cannot be directly titrated by permanganate owing to a secondary reaction between the permanganate and acid, but if one of a class of certain metallic compounds (manganous sulfate, lead chloride, mercuric sulfate, etc.) is present in considerable amount, the extent of this secondary reaction is minimized, though the red coloration showing the end-point is far more fugitive than in their absence; the deep yellow color of ferric chloride, tending to obscure the end-point, may be lightened by the addition of phosphoric acid. The time of reduction may be cut down to a few minutes by passing the ferric solution through a Jones' reductor.

B. By standard potassium bichromate. In titrating by this reagent the equation is

$$6FeCl_2 + K_2Cr_2O_7 + 14HCl = 3Fe_2Cl_6 + 2KCl + Cr_2Cl_6 + 7H_2O.$$

no reaction taking place between dilute hydrochloric acid and bichromate in the cold.

Since the green and yellow colors of chromic and ferric chlorides will not allow the faint yellow of the excess of bichromate to be seen, the point of entire conversion of ferrous into ferric is denoted by the absence of a blue precipitate or blue coloration when a drop of the titrate is mixed with a drop of a

weak solution of potassium ferricyanide. The latter is spread in drops over a slightly greased porcelain plate, and after each addition of a small volume of the titrand, a drop of the titrate is transferred to one of the ferricyanide and the effect noted. The end-point is a clear brown color.

In titrations by permanganate, at first the red color vanishes immediately below the surface of the titrate, growing more diffusive as the oxidation proceeds, and one can correspondingly diminish the rate of flow, finally to drops only. No such direct indication is afforded by bichromate, yet one can observe in the sequence of tests a gradual diminution in the density of the blue precipitate (ferrous ferricyanide), later the lessening intensity of the blue coloration, and so follow the progress of the oxidation.

As zinc chloride interferes with the reaction with ferricyanide, the reduction is effected by some other reagent. A stream of sulfurous acid or hydrogen sulfide may be passed through the liquid; as any excess of either would reduce bichromate, the liquid is boiled for a sufficient time in a flask provided with a cork and Bunsen's valve, which allows steam to escape but prevents the entrance of air. After cooling, the flask is opened and the titration proceeded with.

A far more rapid process is the reduction of the hot solution by a slight excess of stannous chloride; the excess is then converted into stannic chloride by the addition of mercuric chloride. The reactions are

Fe_2Cl_6 (yellow solution) $+ SnCl_2 = 2FeCl_2$ (colorless solution) $+ SnCl_4$; and $SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2$.

The liquid, now ready for titration, contains stannic, mercuric, and mercurous chlorides, neither of which, in a cold solution, affects bichromate or ferricyanide.

With manganese ores containing but relatively little iron it is better to dissolve a quantity of several grams, precipitate the iron by ammonia, filter and dissolve the ferric hydrate (and whatever manganic hydrate that may have co-precipitated) in hydrochloric acid, and proceed with the solution as usual.

All things considered, the best means of finding the strength of the permanganate or bichromate solutions is by iron wire (page 209). Some would prepare a stock solution of ferric chloride, determine the concentration by a gravimetric process, and for standardization, weigh a suitable volume and continue exactly as with the hydrochloric solution of an ore. By this procedure it is claimed that certain sources of error affecting the assay (*e. g.*, loss through volatility of ferric chloride on boiling the solution) are practically counteracted by corresponding errors during the standardization. But it is highly probable that the errors incurred in gravimetrically determining the iron in the stock solution will be at least as great as those the scheme is intended to rectify; moreover, the losses or gains that would be experienced by a nearly pure ferric solution may be considerably increased or diminished by the soluble constituents of an ore or its gangue. With the latter point in view, others would prepare a large quantity of a finely powdered ore, and assume that the average of a number of determinations made by one or several operators is the true iron-content. This "standard ore" is then used to set the strength of the permanganate or bichromate solutions, observing the precaution of treating it in exactly the same manner as the ores to be assayed. But since all the determinations of iron in the standard ore were presumably made with iron wire or its equivalent as a basis, not only is its intercalation of no avail for correcting the losses or gains referred to, but may per se introduce other errors (from imperfect mixing, segregation, absorption of moisture, etc.) of greater consequence.

Volumetric determination by reduction. A number of reducing agents have been proposed for the titration of ferric solutions, but owing to the instability of the solutions from their ready absorption of oxygen from the air, the methods are not regarded with much favor. Here all the iron in the titrate must be in the form of ferric chloride with no other oxidizer present; any ferrous choride may be oxidized by addition of a slight excess of potassium permanganate, chlorine water, or potassium chlorate to the strongly acid solution, and boiling off the excess of chlorine.

A. Stannous chloride abstracts two atoms of chlorine from ferric chloride—

$$Fe_2Cl_6 \text{ (yellow)} + SnCl_2 = 2FeCl_2 \text{ (colorless)} + SnCl_4.$$

and reduces ferric sulfocyanide to ferrous sulfocyanide—

$$Fe_2(CNS)_6 \text{ (red)} + SnCl_2 + 2HCl = 2Fe(CNS)_2 \text{ (colorless)} + 2HCNS + SnCl_4.$$

When standard solution of stannous chloride is added to a hot acidified solution of ferric chloride the yellow color fades as the reaction proceeds. If when the titrate has become but faintly yellow potassium sulfocyanide be added and the titration resumed, a sudden blanching of the red solution indicates that all the iron has passed to the ferrous state. Some prefer to add at once an excess of stannous chloride and titrate back by standard iodine solution and starch-paste.

Another indicator is due to Campbell; the green hue produced by the addition of a little cobaltous chloride to the ferric chloride solution changes to a clear blue as soon as all the ferric chloride is reduced to ferrous.

B. Cuprous chloride, according to Winkler, has an advantage over stannous chloride in that reduction takes place in the cold as promptly as at higher temperatures, and that after bleaching the sulfocyanide, the next drop of the titrand clouds the titrate with insoluble cuprous sulfocyanide, a confirmation of the former indication. The reagent rapidly oxidizes on exposure, however.

C. Sodium thiosulfate reduces ferric chloride—

$$Fe_2Cl_6 + 2Na_2S_2O_3 = 2FeCl_2 + 2NaCl + Na_2S_4O_6.$$

while thiosulfuric acid is not decomposed by cold, very dilute free acetic acid. The free hydrochloric acid in the solution of the ore is replaced by acetic, by the addition of sodium acetate until the red color of ferric acetate appears, then hydrochloric acid until again light yellow. An excess of standard sodium thiosulfate is run in, and the excess titrated back by standard iodine and starch-paste. Better results are had by the interposition of potassium iodide which reacts with ferric chloride with liberation of iodine. The iodine is then determined by standard thiosulfate and starch-paste.

D. Moralit bases a method on the precipitation of ferric chloride and ferric sulfocyanide by potassium ferrocyanide—

$$2Fe_2Cl_6 + 3K_4Fe(CN)_6 = Fe_7(CN)_{18} + 12KCl.$$
$$2Fe_2(CNS)_6 + 3K_4Fe(CN)_6 = Fe_7(CN)_{18} + 12KCNS.$$

For an indicator he adds ether and a little potassium sulfocyanide to the titrate. The ferric sulfocyanide dissolves in the floating layer of ether, communicating its characteristic red color, while Prussian blue is insoluble. The end-point is the decolorization of the ether. The process is conducted with several precautions.

To standardize reducing volumetric solutions, crystallized ferric ammonium sulfate is suitable; or if ferric chloride is preferred, iron wire may be dissolved in hydrochloric acid, the ferrous chloride peroxidized by potassium permanganate or potassium chlorate, and the solution boiled until all free chlorine has disappeared.

E. A nearly obsolete method is that of Fuchs, who digests a weighed sheet of copper in the ferric chloride solution for several days with exclusion of air. The copper loses in weight according to the reaction $Fe_2Cl_6 + Cu_2 = 2FeCl_2 + Cu_2Cl_2$, 63.6 parts in weight lost by the copper corresponding to 56 parts of iron.

Ferrous oxide. The protoxide of iron may be in an ore in the form of magnetite or allied minerals, or as siderite, or the gangue may contain pyrite, a ferrous silicate, etc. For a determination the ore is dissolved in hydrochloric acid in a flask through which flows a current of carbonic acid gas; after cooling, the solution is immediately titrated by weak standard bichromate. The insoluble matter is filtered off and dissolved in hot hydrofluoric and hydrochloric acids, also with exclusion of air, most conveniently accomplished by placing the residue and acids in a large platinum crucible and heating on a water-bath, the crucible covered by a large funnel into which is passed a current of carbon dioxide. The solution is titrated by bichromate. After titration, any insoluble residue should be inspected for coarse particles of pyrite; if any are found the residue is decomposed by nitric acid and the iron determined.

The results for ferrous oxide in the hydrochloric solution of the ore are in many cases somewhat too low from the fact that most ores, especially the hematites and limonites, contain small amounts of the higher oxides of manganese, such as isomorphous manganese sesquioxide. The author has obtained fair results by washing the ore before dissolving it, with a hot, very dilute solution of oxalic acid, and has detected magnetite in manganese ores by this scheme. When an ore contains certain organic matters, a part of the ferric chloride is reduced to ferrous and the results are correspondingly high; here it is well to endeavor to wash out the organic matter by some organic solvent, or to remove it by elutriation with water or a heavier neutral liquid.

Silica and bases. The proximate constituents of an ordinary iron ore may be divided as regards solubility into two classes.

A. Soluble in hydrochloric acid. Ferrous and ferric oxides and ferrous carbonate, manganese oxides, calcium and magnesium carbonates, calcium sulfate, calcium phosphate, and the silica and bases of certain silicates.

B. Insoluble in hydrochloric acid. Crystallized and amorphous silica, crystallized titanic acid, and many silicates that may contain as bases iron, manganese, aluminum, calcium, and magnesium oxides and the alkalies.

No sharp line can be drawn as to the deportment of certain compounds such as pyrite, aluminum phosphates, titanates, organic matter and the like, as according to the fineness of the powder, strength of acid, time of digestion, and other considerations, they may pass entirely or partly into solution, or remain insoluble.

Hence in the analysis of an ore the only safe course is to first treat the powder with hydrochloric acid, and after filtering, decompose the residue by fusion with sodium carbonate. The melt is disintegrated by water, dissolved in hydrochloric acid, and united with the original solution. After removing silica, the bases are separated seriatim in the following order: iron and aluminum, manganese, calcium, magnesium. Determinations of the alkalies, titanic acid, sulfur and sulfuric acid, combined water, organic matter, etc., are made on separate portions of the ore.

Silica is determined by evaporating to dryness the solution obtained as above; on taking up by dilute hydrochloric acid, usually only silica remains, but in some ores it may be contaminated by titanic acid or (rarely) tungstic acid. In this case the residue may be evaporated with hydrofluoric and sulfuric acids, ignited, and the weight of the residue deducted from the previous weight.

A lean (highly siliciqus) ore within certain limits of composition is decom-

posed on heating to bright redness, with the formation of silicates easily decomposed by hydrochloric acid, the silica gelatinizing; on evaporation and resolution the silica is left in a nearly pure condition.

In presence of much ferric or aluminic chloride silica can hardly be made entirely insoluble by one evaporation and heating of the residue, and the silica remaining on resolution in acid is apt to be very impure.

Alumina. From the similarity of their reactions, ferric and aluminic compounds generally accompany each other in the process of separating other bases. The separation of aluminum from iron is here the more difficult from the relatively large amount of the latter. The simple means of precipitating the iron by potassium or sodium hydrate leaving the alumina in solution, is imperfect, even when the iron has been previously reduced to the ferrous state, and the precipitate becomes granular tetroxide; when the two are precipitated by ammonia as mixed hydrates, ignited to oxides, fused with sodium carbonate and the melt lixiviated by water, much alumina is retained in the ferric oxide; and the indirect method of weighing the mixed sesquioxides, redissolving and determining the iron volumetrically and the alumina by difference is never satisfactory. The following methods give fair to good separations.

1. Sodium thiosulfate added to a boiling slightly acid solution containing much phosphoric acid, precipitates aluminum phosphate mixed with sulfur, while iron is only reduced to a ferrous salt. Carnot believes that the reaction is favored when the only free acid in the solution is acetic. The precipitated aluminic phosphate is dissolved in hydrochloric acid, filtered from sulfur, reprecipitated, and finally weighed as the phosphate $Al_2O_3P_2O_5$. The reaction with thiosulfate is $Al_2(SO_4)_3 + 3Na_2S_2O_3 = Al_2O_3 + 3S + 3SO_2 + 3Na_2SO_4$.

2. Iron in not too large an amount may be precipitated electrolytically on a cathode of platinum,* or in any amount on one of mercury, forming an amalgam.†

3. If the concentrated solution of the chlorides be saturated with gaseous hydrochloric acid and mixed with an equal volume of ether, the aluminum is precipitated as granular $Al_2Cl_6.12H_2O$.‡

4. Borntrager § takes advantage of the solubility of ferric oleate in petroleum. After neutralizing the solution of ferric and aluminic chlorides with potassium hydrate, the oleates are precipitated by neutral potassium oleate, filtered and dried. The ferric oleate is then lixiviated by hot kerosene and the residual aluminum oleate calcined to alumina and weighed.

5. Other methods have been proposed, based on the precipitation of the iron by an excess of trimethylamin; the relative insolubility in water of basic ferric nitrate as compared to that of basic aluminic nitrate; precipitation of the iron by nitroso-beta-napthol; etc.

Manganese. After the separation of the ferric and aluminum oxides from the other bases by ammonia or an acetate, the manganese in the filtrate is thrown down by ammonium acetate and bromine followed by ammonia; on boiling, all the manganese separates as flocculent hydrated binoxide. The lime and magnesia usually found in iron and manganese ores complicate matters, since the precipitate is prone to carry down these bases in considerable amount.‖ Probably the best plan for their removal from the precipitate is to dissolve it in hydrochloric acid, neutralize the solution by ammonia, and precipitate the manganese

* Journ. Anal. Chem. 3—91 and 4—488.
† *Idem*, 5—627.
‡ Am. Journ. Sci. 52—416.
§ Zeits. anal. 32—187.
‖ Chem. News, 1889—2—262.

as sulfide; a less tedious process is that of neutralizing the hydrochloric solution of the precipitate by ammonia, adding a sufficiency of ammonium acetate, and again precipitating the manganese by bromine and ammonia.

If small in quantity the manganese binoxide may be ignited until it has passed to the tetroxide (Mn_3O_4) and weighed; but if considerable in amount it is better to redissolve and determine as pyrophosphate.

Where the manganese of an ore is not too small in amount the state of oxidation can be found by one of the methods of chlorimetry that recognizes the presence of ferrous oxide.

Lime and *magnesia* are determined in the filtrate from the manganese binoxide by the usual methods for these bases, precipitating the calcium as oxalate, and in the filtrate the magnesium as ammonium magnesium phosphate. Where many analyses are in hand the oxalate of calcium may be dissolved in hydrochloric acid and the oxalic radical titrated by standard permanganate; and the ammonium magnesium phosphate dissolved in standard acid and the excess titrated back by standard alkali.

Phosphorus is determined by dissolving the ore in hydrochloric acid and proceeding substantially as in the determination of this element in steel, but as all the phosphorus of an ore is already combined with oxygen as phosphoric acid, the precaution of evaporating the solution and heating the residue is here unnecessary. Usually combined with calcium (as apatite), there are often found other combinations that are insoluble in acids, so that the residue from the solution of the ore in hydrochloric acid should be examined for phosphorus, though this precaution may be omitted for ores from certain localities that are known to contain all the phosphoric acid in soluble combinations. Simply igniting the insoluble residue of some ores or grinding it to a fine powder will so attenuate the particles or alter the combination of the phosphoric acid by inter-reactions, that all the acid may be dissolved out by heating the residue with strong hydrochloric acid. In ores where all the phosphoric acid is as apatite, nearly or quite all may be extracted by simply boiling the ore with dilute nitric acid.

Sulfur may be in the gangue as iron disulfide, sulfate of calcium, etc., and for its determination the ore is dissolved in hydrochloric acid containing nitric acid or other oxidizer. Calcium sulfate is soluble in dilute hydrochloric acid, but if barium sulfate is suspected, the insoluble residue should be fused with sodium carbonate, the alkali sulfate lixiviated by water, the filtered solution acidified, and the silica separated by evaporation. The sulfuric acid in the united filtrates is precipitated by barium chloride and weighed as barium sulfate in the usual way.

The sulfur existing in the gangue as pyrite or arsenopyrite and that as calcium or barium sulfate may be approximately distinguished as follows: The finely powdered ore is digested with a strong solution of ammonium carbonate and filtered; in the filtrate is ammonium sulfate due to the reaction between the ammonium carbonate and calcium sulfate. From the residue the calcium carbonate and any barium carbonate are dissolved out by cold dilute hydrochloric acid. Now containing pyrite and barium sulfate, the residue is fluxed by sodium carbonate and nitrate, lixiviated by water, and the sulfuric acid in the filtrate and the barium in the residue determined. A simple calculation will distribute the sulfur among these compounds.

Arsenic is sometimes found in ores, and precipitates more or less completely along with phosphoric acid when the latter is thrown down by molybdic acid; magnesic solution also precipitates arsenic acid as ammonium magnesium arsenate. Arsenic may be removed from the hydrochloric acid solution of

an ore by evaporating two or three times with oxalic and hydrochloric acids, it volatilizing as arsenic chloride.

In Pattinson's * method the hydrochloric solution of the ore is treated with sodium thiosulfate to reduce ferric chloride, the sulfurous acid boiled off, and the cooled solution strongly acidified by hydrochloric acid. Powdered zinc sulfide is stirred in to precipitate the arsenic as sulfide, which is then filtered off and determined by direct weight or otherwise. The filtrate is mixed with a little ferric chloride and an excess of calcium carbonate; ferric hydrate and phosphate are precipitated, and after filtering may be dissolved and the phosphorus determined as in the acetate process.

Another method is based on the volatility of arsenic chloride. The ore is brushed into a flask, moistened with nitric acid and heated to decompose arsenopyrite, and distilled with concentrated hydrochloric acid and ferrous sulfate. The distillate is received in water and the arsenic precipitated by hydrogen sulfide, the arsenic sulfide washed with carbon disulfide to extract free sulfur, dried and weighed.

Titanic acid. The minerals menaccanite, rutile, sphene, and anatase are frequent associates of magnetic ores, but are seldom met with in other varieties. From the negative character of titanium compounds the determination is not an easy matter. The native oxides are insoluble in hydrochloric or nitric acid, but dissolve in melted potassium hydrofluoride, and in hot concentrated sulfuric acid best applied in the form of melted sodium or potassium pyrosulfate.

The methods for separation from bases apply the insolubility of sodium titanate in water, the precipitation of titanic acid from its solution by ammonia, or the precipitation of beta-titanic acid on boiling a dilute solution containing but a very small proportion of free acid, especially a mineral acid. The most common method is to get all the bases of the ore as sulfates, either by direct fusion with sodium pyrosulfate or otherwise, and the titanium as sodium titanate. After dissolving in a large volume of cold water and filtering, the ferric sulfate is reduced to ferrous sulfate (to prevent the decomposition of the former compound and precipitation of ferric hydrate on boiling); sulfurous acid is a convenient reagent for the reduction. The solution is nearly neutralized, then boiled for some time. The precipitate of titanic acid, containing some iron oxide and a (usually inconsiderable) amount of phosphoric acid, is fused with a pyrosulfate and the above treatment repeated; now nearly pure, it is ignited and weighed as titanium dioxide.

In Classen's method, the hydrochloric solution is mixed with hydrogen peroxide and the iron precipitated by potassium hydrate; the titanium remains in solution as the trioxide (TiO_3). An aliquot part is filtered off and boiled until the hydrogen peroxide is decomposed, part of the easily reducible titanic trioxide separating at the same time. After acidifying and heating until the trioxide has been reduced to the binoxide, the latter is precipitated by a very slight excess of ammonia. After weighing, the precipitate should be examined for alumina and silica.

A volumetric method is founded on the reduction of titanium dioxide to titanium sesquioxide, which may then be reoxidized by standard potassium permanganate. The reducing agent is metallic zinc, and the process is the same as for the determination of iron, except that the titrate must be carefully shielded from the air on account of the far greater susceptibility of titanium sesquioxide to oxidation. The volume of the titrand used in the titration is that required for the oxidation of both the titanium sulfate and the ferrous sulfate that may be present, and to determine the latter, the titrate is treated with

* Journ. Socy. Chem. Ind. 12—119.

hydrogen sulfide, this reagent reducing only the ferric sulfate. A second titration is made, and the difference is the volume of permanganate oxidizing the titanium sesquisulfate—

$$5Ti_2(SO_4)_3 + K_2Mn_2O_8 + 9H_2SO_4 = 10Ti(SO_4)_2 + 2KHSO_4 + 2MnSO_4 + 8H_2O.$$

A colorimetric method suitable for the small proportions found in marketable ores, applies the intense yellow color produced when (fluorine-free) hydrogen peroxide solution is added to a solution of titanium sulfate. The standard is a sulfuric solution of pure titanic acid.

The determination of phosphorus is interfered with by titanic acid; if the hydrochloric solution be evaporated to dryness a compound of ferric oxide, titanic acid and phosphoric acid remains insoluble with the silica; in precipitating titanic acid by boiling the dilute solution, part or all of the phosphoric acid is also carried down; and it is said that the presence of titanic acid in a nitric solution prevents the complete precipitation of phosphoric acid by molybdic solution.

After fusion of a mixture of the two acids with sodium carbonate and lixiviation of the fusion by hot water, sodium phosphate passes into solution, while all the titanium remains in the residue as acid sodium titanate. In the method of Jennings, the ore is treated with hot concentrated hydrochloric acid, and, without filtering, the liquid neutralized and the ferric chloride nearly reduced to ferrous chloride by sulfurous acid; then acetic acid is added and the liquid boiled. The residue and precipitate, containing all the phosphoric acid as ferric phosphate, is fused with sodium carbonate and the melt lixiviated by hot water—sodium silicate, aluminate, and phosphate dissolve. The phosphorus is then determined in the filtrate by one of the usual methods. A simpler plan is to flux the ore at once with sodium carbonate, plus a little nitre to oxidize ferrous compounds and organic matter, then lixiviate with water.

Volatile at a red heat. On ignition to bright redness an ore loses combined water, carbon dioxide and organic matter, and about one-half of the sulfur of pyrite. Unless it is deemed advisable to examine further, the result is put down as "volatile at redness" or shortly "volatile matter." Reduction of ferric to ferrous oxide by organic matter, and loss of oxygen by a higher oxide of manganese may increase the result, and oxidation of magnetite or siderite may decrease it.

The separate determination of *combined water, organic matter* and *carbon dioxide* can be done as follows. A portion of the ore is decomposed by hot dilute sulfuric acid in a closed flask and the carbon dioxide led first through a condenser to remove most of the aqueous vapor, then through a calcium chloride drying tube, and finally into a weighed potash bulb to absorb the carbon dioxide, determined by the increase in weight. The water of composition of the mineral and gangue is determined by igniting the ore (previously dried at 100°), in a current of dry air, catching the moisture in a weighed calcium chloride tube. The carbon of organic matter by igniting the ore in a current of oxygen and absorbing the carbon dioxide in a weighed potash bulb following a drying tube; from the increase in weight of the bulb is deducted the weight of the carbon dioxide found by treatment with an acid. An approximation to the amount of organic matter may be had by assuming it to be bituminous in character and to contain about 75 per cent of carbon.

Hygroscopic water is found from the loss sustained in drying the ore at 100°. Since the percentage of moisture is usually decreased, sometimes increased, by pulverizing and exposure to the air, the determination is the more reliable the less manipulation the sample has undergone previous to the drying. For large shipments of ore a weight of from 100 to 2,000 lbs. is a suitable quantity.

COAL.

The coals are amorphous minerals, black or brown in color, of a specific gravity ranging from 1.2 to 1.8, and hardness from .5 to 2.5. According to Balzer, coals are mixtures of complex carbon compounds of a genetic and possibly homologous series. Carbon is the predominating constituent, while all varieties contain more or less hydrogen, oxygen, and small amounts of combined or occluded nitrogen, and hygroscopic moisture. As associates are commonly found slates, calcite, fire-clay, pyrite or marcasite, gypsum, etc.

The different varieties may be enumerated as follows, though no sharp lines divide them, one variety merging into another.

1. Brown coal, lignite, and peat coal are incompletely carbonized woody fiber and therefore contain an unusually large proportion of oxygen (up to 30 per cent) and moisture. Their general appearance and lightness are characteristic, and also their comparative susceptibility to the action of chemicals.

2. Cannel (candle) coal by its close grain and dull fracture suggests an indurated wax. The proportion of moisture is low, as is that of fixed carbon, while the volatile hydrocarbons may be as high as 70 per cent. The sulfur and ash are usually very moderate.

3. Bituminous coal is black, with a fracture that is flat, somewhat resinous in luster, and often iridescent. The layers are frequently interstratified by films of pyrite or calcite. In composition the moisture ranges from 1 to 5 per cent, volatile hydrocarbons from 30 to 45, fixed carbon from 40 to 60, and ash from 2 to 20. The sulfur is seldom below 1 per cent and may reach 5 or more.

A coking or caking coal is one that on slow destructive distillation leaves a hard, dense, lustrous, strongly coherent cellular residue, coke.

4. Semi-bituminous coal is intermediate between bituminous and anthracite and therefore contains more fixed carbon than the former and less volatile matter and moisture.

5. Anthracite is distinguished by its superior hardness and conchoidal or sub-conchoidal fracture, a high resistance to chemicals, and slow smokeless combustion. The purest varieties, including the so-called graphitic anthracite, are little else than carbon with a few per cents of earthy impurities.

Alcohol, ether, chloroform, phenol, and solutions of potassium permanganate and oxidizers generally, dissolve out small variable proportions of organic constituents. Treated with dilute hydrochloric acid and potassium chlorate a coal becomes brown and increases in weight through oxidation. A mixture of concentrated sulfuric and nitric acids dissolves on long digestion a considerable portion from bituminous coal, which is precipitated on dilution. The residue of "nitro-coal" contains more volatile matter than the original and deflagrates slightly on heating; it is largely soluble in solution of sodium hydrate.

The object of an analysis of a given coal may be for information in respect to (1), geological or mineralogical investigations; (2), heat of combustion, for furnace purposes or steaming; (3), the volume and composition of combustible gases yielded on destructive distillation, either without access of air or with a limited supply of air and steam; or (4) for special technical purposes. The character of the analysis and the methods chosen must therefore be adapted to the end in view.

PROXIMATE ANALYSIS.

Here the moisture is expelled by drying the coal, and the volatile hydrocarbons by ignition at a red heat; the remaining carbon is burned in air, leaving the ash. The sulfur of the coal is usually also determined, and occasionally the phosphorus, nitrogen, etc., these in separate portions of the coal.

1. *Hygroscopic moisture* of the coal and gangue. The usual method is to heat one gram of the powder in a crucible or small dish to 100° for one hour and call the loss in weight the moisture. Some writers direct a temperature of 108° and limit the time of heating to fifteen minutes; the Committee of the American Chemical Society on Coal Analysis recommends a temperature of from 104° to 107° for one hour, the coal to be contained in an open porcelain or platinum crucible, and the heat furnished by a toluene-bath. Some coals begin to increase in weight if the drying be prolonged beyond an hour, probably from oxidation of pyrite; it is said that at 100° some of the most volatile hydrocarbons may escape, though this statement lacks confirmation.

The percentage of moisture as determined by this process is a function not only of the hygroscopic capacity of the coal but also of the fineness of the powder and the condition of the atmosphere at the times of weighing, and cannot safely be assumed to represent the average water-content of the coal in the massive state. Hence for a comparison of several coals of the same variety, some would eliminate the moisture entirely from the analyses and report the percentages of the other constituents referred to the coals dried at 100°. A more rational determination of moisture is had by drying a weight of say a ton of coal, observing the usual precautions against loss or gain of moisture during the breaking of the lumps to small fragments. The results of the ordinary analysis are calculated to the basis of this determination by means of the formula $M' = M\frac{100 - W'}{100 - W}$ where W is the percentage of moisture in the finely powdered coal, and W' that in the large sample; M, the percentage of any constituent in the analysis, and M' the percentage in the corrected analysis.

2. *Matter volatile at a red heat.* About one gram of the undried coal is placed in a small platinum crucible provided with a well fitting cover. The covered crucible is heated over a Bunsen burner for exactly three and one-half minutes, then, without cooling, over a blast-lamp for the same time. The temperature and time of heating have considerable influence on the result, hence the specific directions.

The loss in weight of the coal is conventionally considered as due to the expulsion of the volatile hydrocarbons and carbohydrates, plus the moisture as determined in (1) which is to be deducted. But in addition the weight is diminished to some extent by the expulsion of (1), a portion, approximating one-half, of the sulfur of the pyrites or marcasite; (2), any free sulfur; (3), the combined water of gypsum and hydrous silicates; (4), the carbon dioxide of calcite; (5) the escape of particles of coal carried out with the gases, considerable in the case of some 'dry' coals; (6), the combustion of a small amount of the fixed carbon by air entering the crucible, or possibly from a reaction with gypsum. On the other hand, the expulsion of the hydrocarbons is probably never complete on account of the dissociation of a part at a bright red heat with separation of carbon.

3. *Fixed carbon.* There remains from the above ignition a mixture of carbon, ferrous sulfide, and the dehydrated gangue. The form may be that of a loose powder indicating a non-coking coal, or as a swelled hard spongy mass indicating a coking coal; if between the two, no positive conclusion can be drawn as to which class the coal belongs.

The carbon is burned in the open crucible in which a small stream of oxygen may be introduced to hasten combustion. The loss in weight is the fixed carbon, the result increased by the loss of the remainder of the sulfur of pyrite and possibly some of the oxygen of the gypsum, and decreased by the conversion of the iron of the pyrite to the sesquioxide.

4. The *ash* of the coal remains as a soft or gritty powder, tinted yellow or brown in proportion to the content of free ferric or manganic oxide. The composition varies greatly, but is mainly silica and alumina, with oxides of iron, calcium, magnesium and manganese, and calcium sulfate. For metallurgical purposes an analysis of the ash may be made according to the usual process for silicates insoluble in acids, obtaining sufficient material by calcining several grams of the coal.

5. *Sulfur.* For the determination of this most important impurity several methods have been proposed. Those most in use are the fusion or fluxing method and that of Eschka.

A. In the former one gram of the powdered coal is intimately mixed with ten grams of sodium carbonate and five grams of potassium nitrate; the mixture is heated to fusion in a capacious platinum crucible, when by the oxidizing action of the nitrate the carbon burns to carbon dioxide and the sulfur to sulfuric oxide. At the same time the sodium carbonate fluxes the silicates and converts the gypsum to calcium carbonate; the iron is oxidized to ferric oxide. When cold, the mass is treated with hot water and filtered. The filtrate contains all the sulfur as sodium sulfate, and after acidification, is precipitated by barium chloride. Since there is always some or all of the silicate of sodium in the lixiviation, it is more prudent to evaporate the acidified solution to dryness and redissolve and filter before precipitation.

In another method one-half gram of the powdered coal in a small platinum dish is mixed with three grams of sodium peroxide, a little water added, and the liquid evaporated to dryness and ignited. The evaporation and ignition are repeated with other portions of the peroxide, when all the oxidizable matters should have been oxidized. The residue is boiled with water, filtered, acidified and precipitated as usual.

The greatest objection to fusion methods is that the solution from which the barium sulfate is precipitated contains large amounts of sodium chloride. For this reason the following method devised by Eschka has largely displaced them.

B. One gram of finely powdered coal is mixed with one-half gram of sodium carbonate and one gram of powdered magnesia (levis) and gradually heated in a platinum crucible or dish over a sulfurless flame with frequent stirring, until the color shows that all the carbon has been consumed. The crucible is cooled, a gram of solid ammonium nitrate stirred in, and the crucible reheated until the latter is volatilized. The mass remains as a powder, and is transferred to a beaker and boiled with water, filtered, and the sulfuric acid precipitated from the filtrate.

The rationale of the process is that the carbon is burned in intimate contact with the alkali carbonate which immediately fixes the sulfur dioxide or trioxide liberated during the combustion. To facilitate the burning of the coal there is admixed a large bulk of some infusible inert powder, here magnesia. The ammonium nitrate is introduced to oxidize any traces of unburnt carbon and to convert any sodium sulfide or sulfite to sulfate. On lixiviation there passes into solution sodium sulfate and the excess of carbonate, also calcium sulfate if it should not have been entirely decomposed by the heating with sodium carbonate in the crucible or with the solution during the lixiviation. With

coals high in sulfur the residue insoluble in water may retain a small amount and should be dissolved in dilute hydrochloric acid, filtered, and the filtrate tested by barium chloride.

The reagents should be examined for sulfur compounds by igniting a mixture of ten grams of magnesia, ten grams of ammonium nitrate, and five grams of sodium carbonate, boiling with water, filtering, acidifying, and precipitating by barium chloride; if any barium sulfate falls it is weighed and one-tenth the weight deducted from each analysis.

A modification of the above directions, somewhat more convenient, dispenses with the ammonium nitrate, and effects the oxidation to sulfate by the addition of bromine water to the lixiviation — one cubic centimeter of the saturated solution is usually sufficient. It will be noticed that on mixing the reagent with the alkaline solution the bromine reacts with the alkali, and the solution remains colorless, but on acidification the bromine is regenerated and the solution becomes light yellow. To dissolve the ignition at once in hydrochloric acid containing bromine, as has been proposed, is objectionable for the reason that not only the magnesia but a part of the constituents of the ash as well enter the solution and may impurify the barium sulfate.

Hundeshagen* urges the substitution of potassium carbonate for the sodium carbonate on the ground that its reactive power is superior in that it requires a higher heat for dehydration; the assertion is not confirmed by Handy.†

Antony and Succhesi propose that one gram of coal be mixed with four grams of manganese binoxide and two grams of sodium carbonate. After ignition for a half-hour, the mass is treated with dilute nitric acid, boiled, filtered, and the sulfuric acid precipitated as usual. They claim a more rapid combustion results from the substitution of the manganese binoxide for magnesia ($3MnO_2 + C = Mn_3O_4 + CO_2$).

Atkinson's method is similar to Eschka's, differing in that the coal is mixed with five parts of dry sodium carbonate and heated in a platinum dish for an hour, preferably in a muffle. The sodium carbonate should not sinter or fuse. The sodium sulfate formed and the excess of sodium carbonate are lixiviated by water, filtered, acidified and precipitated by barium chloride as usual. Neilson obtained good results by burning coal in contact with calcium carbonate alone, dissolving in hydrochloric acid, and precipitating; some loss was experienced in lixiviating with water alone. He proposes to mix the coal with sodium carbonate and manganous carbonate, heat and finally fuse, the manganese passing to oxide and acting as a carrier of oxygen; the melt is dissolved in acid, evaporated and precipitated.

C. Fuming nitric acid, nitro-hydrochloric acid, and other strong oxidizers have been used on the presumption that all the sulfur can be extracted by them, but it appears well established that a complete oxidation of the carbon is essential to a complete liberation of the sulfur. Many coals are completely, though slowly, oxidized by potassium chlorate in conjunction with nitric acid, but the process offers no particular advantages over others more speedy and certain.

Sulfur may exist in coal in at least five states of combination: (1) as pyrite or marcasite, sometimes in dark streaks hardly to be distinguished from the coal itself; (2) as gypsum, rarely as barite; (3) as an organic compound;‡ (4) as basic ferric sulfate ("misy") coming from decomposition of pyrite by moist air; (5) rarely as free sulfur (in weathered pyritic breeze). It is often of practical interest to know the combinations in which the sulfur of a given

* Chem. News, 1892—2—169.

† Journ. Socy. Chem. Ind. 6—360.

‡ Chem. News, 1888—2—65.

coal exists and a number of plans for their differentiation have been brought forward. None can be considered satisfactory, however.

The sulfur combined as calcium sulfate or barium sulfate is left in the ash on burning the coal in oxygen at a heat high enough to decompose any sulfate of iron formed from pyrite. If, however, the coal contains calcite, too high a percentage of calcium sulfate will be found, due to a reaction with pyrite. Or the calcium sulfate may be transformed to carbonate by digestion with sodium carbonate, and the sulfuric acid passing into solution determined, yet here some of the finely divided pyrite may also be attacked. On the other hand if it is sought to oxidize and extract the pyrite by a mixture of bromine and solution of sodium hydrate, some of the calcium sulfate may also be dissolved.

6. *Phosphorus* is to be looked for in fuel employed for the smelting of Bessemer iron ores — it is seldom higher than .1 per cent. Lynchenheim* burns a coal or coke in a shallow platinum dish, then fuses the ash with sodium carbonate and nitrate. The fusion is dissolved in hydrochloric acid, the bases converted to nitrates by evaporation with nitric acid, and after filtering from the silica, the phosphoric acid is precipitated by molybdic solution and determined as in an iron ore (page 356). *Titanic acid*, a rare constituent of the gangue, may be brought into solution by fusing the ash with an alkali pyrosulfate, then proceeding for its determination as directed for an iron ore.

As might be expected from the origin and nature of coal, various gases are occluded. Bedson,† by heating in vacuo 670 grams of coal dust to 100°, obtained 753 cubic centimeters of a mixture of gases, mainly nitrogen, paraffins of the C_nH_{2n+2} series, and carbon dioxide.

Calculation. As in every analysis where one constituent is determined by difference, the total percentage of the proximate analysis of a coal is exactly 100. The proper location of the sulfur is a problem, since the organic combinations of sulfur presumably pass off entirely with the matter volatile at a red heat, the sulfur of the pyrite partly in the volatile matter and partly in burning the fixed carbon, while that of the gypsum remains in the ash. Since it is not customary to carry the examination so far as to attempt to distinguish the combinations of sulfur, various plans for distributing it have the sanction of different writers. Some would deduct one-half the sulfur from the volatile matter and one-half from the fixed carbon, arguing that pyrite is the predominating combination of sulfur in the ordinary run of coals. Others would deduct one-third from the volatile matter, fixed carbon, and ash respectively. Still others would make no attempt to locate the sulfur, allowing each of the results on the other constituents to retain whatever proportion may be included, and report the total sulfur separately. There are manifest objections to all these schemes.

It will be apparent from the foregoing that a proximate analysis follows the lines of the manufacture of coke, yet the differences in temperature and time of heating, size of particles, admission of air, etc., are so great as to advise caution in pronouncing on the quality of a sample of coal for this purpose from an analysis alone. As a rule the yield of coke from the beehive oven is considerably greater than that indicated by the percentage of fixed carbon and ash found by analysis.

The analysis of other fuels consisting mainly of fixed carbon, such as charcoal, coke, or anthracite, is performed in practically the same way as that of a coal. Meade and Attix‡ note that of the matter volatile at redness when a

* Trans. Amer. Inst. Mining Engrs. 19—66.

† Chem. News, 1893—2—187.

‡ Journ. Amer. Chem. Socy. 1899—113.

coke is heated in the conventional analytical scheme, the loss in weight due to combustion of carbon by air in and entering the crucible may be several times the weight of true volatile matter, and advise that the heating be done in a current of nitrogen or hydrogen, or that a correction be applied, found by again heating the crucible after the determination in the usual way, when the carbon burned by the air is practically the same as during the previous ignition.

For the valuation of a coal for the manufacture of illuminating gas a test following the manufacturing process is in use at some gas works. Three samples of 2.24 lbs. each (1-1000 of a gross ton) are submitted to distillation. The retort is of iron, of the form of a muffle five inches wide, four high, and twenty-six long. It is heated to bright redness in a furnace and the sample introduced. The temperature is maintained as uniform as possible. The gases rise in a wrought iron pipe two inches in diameter, and pass over into a condenser, a battery of twelve vertical pipes 1.5 inch in diameter and 42 inches long, which serves to liquefy the tar and gas-liquor. Thence the gas passes through a scrubber where water takes up ammonia and sulfurous acid, thence to a purifier containing lime or ferric oxide to remove sulfur compounds, finally to a gasometer. The quality of the gas is tested by a Bunsen's photometer and analysis, the tar, gas-liquor, and ammoniacal water are collected and measured, and the coke weighed. The yield of gas from a good quality of coal is about twelve cubic feet.

Ultimate Analysis.

The *ultimate analysis* of a fuel presents no great differences from the elementary analysis of other solid sulfurous organic bodies (page 298). From the difficulty of oxidizing the refractory coke or residue of fixed carbon, the combustion is best made in a current of oxygen. The coal is contained in a tared platinum or porcelain boat so that the ash can be weighed and further examined if desired. The sulfur and phosphorus are determined as described before. The oxygen is found by difference, subtracting from 100 per cent the sum of the percentages of the carbon, hydrogen, nitrogen, ash, and (assuming that all the sulfur of the coal is combined as pyrite) five-eighths of the percentage of sulfur.

(Pyrite on ignition in oxygen or air passes to iron sesquioxide which remains with the ash. Hence from 100 there should be deducted the percentage of pyrite *less* the resulting iron sesquioxide which has already been deducted as part of the ash. The difference between the pyrite and sesquioxide is five-eighths of the total sulfur, since pyrite (FeS_2, 120.14) contains two atoms of sulfur (64.14), and two molecules of pryrite (240.28) yield one molecule of ferric oxide (Fe_2O_3, 160). Hence, calling the percentage of sulfur S, we have $S\frac{120.14}{64.14} - S\,\frac{120.14}{64.14} \times \frac{164}{240.28} = \frac{5}{8}\,S$ as the difference).

The calorific power of a fuel may be computed from the ultimate analysis according to the formula of Dulong —

$$\text{Calorific power} = 8080\ C + 34460\ (H - \frac{O}{8}) + 2250\ S.$$

The determination by means of the calorimeter is deserving of more attention than has been accorded in the past, especially since there are several calorimeters on the market that in careful hands are capable of furnishing reliable data. A practical burning test may well supplement the analysis of a coal, conducted of course under as nearly as possible the conditions that will

obtain in practice, and in association with a similar experiment on a coal of standard quality.

The specific gravity of a coal, and the porosity and resistance to crushing of a coke or charcoal may be required for metallurgical purposes. The apparent and true specific gravities and the volume of the pores in proportion to the solid matter are calculated from the weight of a lump, (a) after drying; (b) weighed in air, the pores filled with water; (c) weighed in water, the pores filled with water.

NATURAL WATER.

Natural waters contain in solution various inorganic bases and acid radicals and dissolved gases, frequently also organic matter and suspended particles. Almost invariably are found lime, magnesia and the alkalies, combined with carbonic and sulfuric acids, and often chlorides, ferrous bicarbonate, silica, hydrogen sulfide, and in small quantities alumina, the rarer alkalies, bromine and iodine, phosphoric acid, etc. If polluted by sewage there are found nitrogenous organic matter, ammonia, nitrates and nitrites. Suspended matter is usually clay, sand or limestone grit, sometimes vegetable matter.

The character and proportions of the inorganic impurities may vary enormously.* A few examples are given.

A spring water from Sandstone, Minn., contained total solid matter 4.18 grains per gallon, of which 1.60 grains were calcium carbonate, .85 grain magnesium carbonate, and .40 grain silica.

The Kent (potable) water of London contained 30 grains per gallon of solid matter, of which 16 grains were calcium carbonate, and 5 grains calcium sulfate.

The Hathorn Spring (medicinal) of Saratoga, N. Y.; total solids 888 grains, of which 510 are sodium chloride, 176 magnesium carbonate, and 11.45 lithium carbonate.

The Atlantic Ocean; total solids 2140 grains, of which 1671 are sodium chloride, 200 are magnesium chloride, 108 potassium sulfate and 31 sodium bromide.

The Dead Sea; total solids 13489 grains, of which 1703 are sodium chloride, 4457 magnesium chloride, 1377 calcium chloride, and 683 potassium chloride.

The analysis of a water should in every case include a determination of the total solid matter, dissolved and suspended. Beyond this the procedure diverges, the course depending on the use to which the water is to be put. If for steaming, the nature and proportions of the inorganic solids will decide as to the liability of the water to corrode the iron of the boiler, to foam on boiling, or to deposit scale. If for drinking, the presence of pathogenic germs or the environment suitable for their growth is indicated by an undue amount of certain constituents characteristic of animal refuse or decaying vegetable matters. Certain organic or inorganic bodies, even in small amounts, will condemn a water for technical and manufacturing purposes. Medicinal waters call for as complete an analysis as practicable.

The usual analytical methods are outlined in the following. The pronounced disadvantages of operating on material in the form of a highly dilute solution are realized in many of the determinations, particularly as some of the constituents are volatilized or altered in composition during evaporation.

A. Analysis for technical purposes.

1. *Color.* A water is classified as to color by viewing a white surface through a standard depth. The observation is made through a tube of glass or porcelain two inches in diameter and twenty-four inches in length, the ends closed by

* Muspratt's Chemistry, 5—133.

disks of colorless glass, one cemented on, the other clamped. The tube is half filled with the water, held horizontally, and the comparison made between the columns of air and water.

For a definite expression of color various standard solutions have been proposed. By Crookes, Odling and Tidy are advised solutions of ferric and cupric salts held in superimposed glass cells, and by Leeds, Nessler's solution tinted by ammonia; but of the former it is found that the color of ferric chloride varies greatly with the acidity of the solutions, and of the latter, that much depends on the temperature and concentration of the Nessler's solution. Hazen recommends a solution of chloroplatinic acid tinged with a cobalt salt, the standard being referred to metallic platinum. Lovibond's tintometer glasses (page 261) are said to be well adapted to the purpose.

The *odor*, if any, is a clue to the origin and present condition of a sample. That of sulfuretted water or one containing decaying animal or vegetable matter is pronounced and hardly mistakable.

The *reaction* with litmus and lacmoid detects the presence of an acid or alkaline salt and whether the acidity is due to carbonic or a mineral acid.

The *specific gravity* of an ordinary water is so near that of distilled water that for a determination at least 500 Cc. is weighed in a light flask, best at a temperature near 4° Cent. Except for mineral and saline waters the specific gravity is not considered of any great importance. Reichert* believes that the *specific conductivity* of a natural water is a characteristic and fundamental property whose determination should be included in every analysis.

2. *Total solids.* From 100 to 1000 cubic centimeters or grams of the water is placed in a tared platinum dish. If the total solids are less than about 500 grains per gallon the water may be measured, if over this amount the better plan is to weigh. Should magnesium chloride be suspected as one of the constituents, one adds a small weighed amount of sodium carbonate to prevent loss by dissociation and volatilization of hydrochloric acid during the evaporation.

The water is evaporated to dryness on the water-bath and the residue heated to from 105° to 180°, the dish cooled in a desiccator and reweighed. Some trouble may be experienced in weighing a deliquescent residue, and for waters of this nature it is better to substitute for the platinum dish a broad glass weighing-bottle with a glass stopper, plain or provided with a stopcock.†

The *suspended matter* consists of earthy debris, clay, sand, limestone, etc., and sometimes organic matter. It is usually filtered off and the clear liquid used for analysis. If at all considerable the filtration is done, best after complete subsidence, through asbestos or a thick tared paper, which is reweighed after drying at 100°. If thought desirable the residue is examined chemically and microscopically.

3. *Loss on ignition.* The diminution in weight on heating the contents of the dish to redness is due to the combustion of the organic matter by the air or nitrates if present, and the loss of carbon dioxide combined with iron oxide, lime and magnesia, and of some water of crystallization of gypsum. The carbon dioxide may be restored by treating the ignited residue with solution of ammonium carbonate, evaporating, and gently heating to remove the excess.

4. *Silica and bases.* The determinations follow substantially the routine of the analysis of a soluble silicate (page 251). The residue left after ignition is treated with hydrochloric acid, evaporated to complete dryness, redissolved in

* Chem. News, 1889—1—180.

† Journ. Anal. Appl. Chem. 4—53.

hot dilute acid, and filtered; the residue is silica, plus insoluble sediment if the water was turbid and had not been filtered previous to evaporation. The filtrate is heated with a few drops of nitric acid to perduce ferrous chloride, and in succession the iron and aluminum are precipitated as hydrates by ammonia, the calcium as oxalate, and the magnesium as ammonium magnesium phosphate. The precipitate of ferric and aluminum hydrates is redissolved after weighing and the iron determined, volumetrically if large in amount, colorimetrically if small (by conversion to sulfocyanide or ferrocyanide and matching against a solution of iron wire in acid and similarly treated).* Manganese is not a common constituent of ordinary waters; if present it may be precipitated by bromine in the filtrate from the iron and aluminum hydrates, calcined to the tetroxide, and weighed.

The alkalies can be determined in the same liquid provided the magnesium has been separated by precipitation by ammonium carbonate instead of ammonium phosphate, but better in another large volume of the water concentrated to a small bulk. The potassium and sodium, and lithium if present, are separated as usual by platinic chloride.

Muck,† in waters containing not more than traces of iron and aluminum, determines the alkalies by evaporating the water with dilute sulfuric acid to convert all the bases to sulfates. To avoid the use of a large excess of sulfuric acid, he moistens the residue from evaporation of the water with a mixture of three drops of sulfuric acid in 100 Cc. of alcohol, then burns off the alcohol and observes whether the residue appears dry; if so, the above is repeated until the residue remains moist, showing a slight excess of sulfuric acid. The residue is gently ignited and weighed, and the weight of the earthy sulfates, calculated from the previous determination of the earths, is deducted; the remainder is the weight of the sulfates of the alkalies.

The most common of the other metallic compounds occasionally found in natural waters are those of lead, copper, zinc, arsenic and chromium. They may come from natural sources or from sewage, and are usually combined with sulfuric acid; lead may be in the form of a metallic powder attrited from lead pipes by sand in the water. Being more or less poisonous or injurious to health, their determination is of importance in potable waters. Usually occurring in minute quantities, a volume of several liters is evaporated; the determinations follow in the main the well known methods for separation and determination.

5. *Acid radicals.* Carbonic acid is invariably present and may exist in three states: (a), "bound," that combined as calcic, magnesic, ferrous or alkali monocarbonate; (b) "half-bound," that combined with the monocarbonates to form bicarbonates, *e. g.*, $CaCO_3.H_2CO_3$; and (c) "free," that simply dissolved in the water and uncombined with a base. The free and half-bound carbonic acid is expelled on boiling the water, the monocarbonates of the earths precipitating almost completely. Following are a few methods for their determination.‡

(1) Total carbonic acid is determined by adding to the water an excess of lime-water, filtering the precipitate after it has crystallized, and weighing as calcium carbonate. Baryta-water has some advantages, but in either case the absorption of carbon dioxide from the air must be guarded against. A volumetric method is possible — a known volume of standard lime-water is used,

* Journ. Socy. Chem. Ind. 8—175.
† Chem. News, 1890—1—38.
‡ Journ. Amer. Chem. Socy. 1901—405.

and after settling, an aliquot part of the clear liquid is withdrawn and titrated back by standard acid. Should however a sulfate other than calcium sulfate be present, it will also react with calcium hydrate (*e. g.*, $MgSO_4 + Ca(OH)_2 = Mg(OH)_2 + CaSO_4$), and another process must be substituted.

(2) Jelowitz' method. To the water in a flask is added neutral calcium chloride solution. The flask is connected by a reflux condenser to drying tubes, and these to a weighed potash-bulb as in a combustion in the wet way (page 303). The water is boiled until the free and half-bound acids pass into the potash-bulb which is then reweighed. After again connecting the train, the water is acidified by sulfuric acid, and the bound carbonic acid boiled out and determined as before.

(3) Vignon's method. On titrating a water by standard calcium hydrate and phenol-phthalein, the point of neutrality is manifested when the free and half-bound acids are saturated. Another volume of the water is boiled until the free and half-bound acids are expelled and the earthy carbonates precipitated; then the calcium and magnesium combined with sulfuric acid and chlorine may be determined by titration with sodium carbonate and phenol-phthalein.

(4) The principles upon which Seyler proceeds are that carbonates show an alkaline reaction toward phenol-phthalein; bicarbonates neutral; and free carbonic acid, an acid reaction. If a water is neutral or acid toward phenol-phthalein, the half-bound equals the bound, and the volatile equals the sum of the bound and free. On the other hand, a water alkaline to this indicator can contain no free acid, and the volatile acid will be less than the fixed by a certain amount determinable by titration with hydrochloric acid and phenol-phthalein until colorless. Free carbon dioxide is determined by titrating with sodium carbonate and phenol-phthalein until faint pink, *i. e.*, until the carbon dioxide has all combined with the carbonate to form bicarbonate.

Chlorine is readily titrated by a weak standard solution of silver nitrate with potassium chromate as an indicator. Usually the water need not be concentrated, but if it contains alkali carbonates which would react with the titrand they are neutralized by first acidifying by nitric acid, then stirring in calcium carbonate, finally boiling to remove carbonic acid. On account of the turbidity caused by the silver chloride and its refusal to clot (it being so small in amount), it is difficult to catch the end-point where yellow changes to red. Mason advises to make up a comparison liquid of a solution in distilled water of sodium chloride (the proper proportion found by a rough titration of the water) and potassium chromate, then run in silver nitrate solution just short of what is required for entire precipitation. This liquid is practically of the same color and turbidity as the titrate near the end-point.

A gravimetric determination of the chlorine as silver chloride is sometimes more accurate than the volumetric method.

Sulfuric acid is precipitated by barium chloride and weighed as barium sulfate in the usual way; it is advisable that the water be somewhat concentrated by evaporation, acidified, and heated to boiling before precipitation. Volumetric methods are rather tedious and not often used. A photometric process is based on a comparison of the density of the cloud produced by the addition of barium chloride to the unconcentrated water with that in corresponding solutions of a sulfate of known concentration.

Free sulfuric acid, often found in waters from the coal measures from the

* Chem. News, 1898—1—46 and 125.

decomposition of pyrite, is determined by titration with a weak standard alkali. Other free acids are sometimes met with in the drainage from factories.

Hydrogen sulfide. Water containing this gas or a sulfide is treated with an excess of a standard solution of arsenious acid, the very insoluble arsenious sulfide precipitating. After filtering, the excess of the arsenic solution is titrated by iodine and starch-paste.

Another method is to add the water from a burette to an arbitrary small volume (a Cc.) of weak standard iodine solution until the yellow color vanishes, this requiring b Cc. of the water. To the solution is added starch-paste, and it is titrated to faint blue by the iodine solution requiring c Cc. Then $a + c$ Cc. oxidizes the hydrogen sulfide in b Cc. of the water. A blank titration is made on $a + b + c$ Cc. of distilled water for a correction for the iodine needed to produce the blue tint.

Hydrogen sulfide reduces ferric sulfate — $Fe_2(SO_4)_3 + H_2S = 2FeSO_4 + S + H_2SO_4$. The water is acidified by sulfuric acid and mixed with an excess of weak standard ferric sulfate solution, then the ferrous sulfate formed is titrated by weak standard permanganate. It is plain that a water cannot be concentrated for a determination of hydrogen sulfide except after making it alkaline by sodium hydrate, and here oxidation is apt to occur during the evaporation.

Phosphoric acid. The water is acidified by nitric acid and concentrated to a small bulk, then boiled with addition of ferric chloride and ammonium acetate. The precipitate contains all the phosphoric acid as ferric phosphate, and is filtered off and dissolved in nitric acid. The phosphoric acid is then precipitated by molybdic solution and the ammonium phosphomolybdate dried and weighed (page 384).

A colorimetric method is based on the yellow hue produced by potassium molybdate in a dilute solution of a phosphate acidified by nitric acid.*

Boracic acid is found in small amount in some waters. In the method of Gooch the water is made alkaline and evaporated to dryness; the residue is moistened with acetic acid and transferred to a distillation flask. The flask is connected to a condenser, this to a receiver containing a weighed amount of calcium oxide which has been slaked and suspended in water. Into the flask is run some methyl alcohol and the mixture distilled to dryness; more alcohol is added and again distilled; this is repeated five times.

The free boric acid in the flask unites with the methyl alcohol to form methyl borate which passes over with the alcohol vapor, and meeting the lime reacts to form calcium borate. When the distillations are over the distillate is evaporated to dryness and the residue strongly ignited, which leaves it a mixture of calcium borate and oxide. The increase over the weight of the lime is boracic acid.

6. *Hardness.* In common parlance waters are distinguished as 'hard' or 'soft' according as they do or do not curdle with soap. To set a numerical rating on this property, Dr. Clark, following Accum, proposed a scale of "degrees of hardness." Although somewhat empirical, the expression represents a definite quality to the layman and for certain purposes gives all the information needed. The process, however, is obsolescent.

Pure water shows an immediate and permanent lather when shaken with a solution of common soap, but when salts of calcium or magnesium are contained, as they are in all natural waters, they react with the soap to form a precipitate of calcium or magnesium stearate, oleate, and palmitate; thus, $CaCO_3.H_2CO_3 + 2Na(C_{18}H_{35}O_2)$ (sodium oleate) $= 2NaHCO_3 + Ca(C_{18}H_{35}O)_2$ (calcium oleate); (free mineral acids also decompose soap, setting free the

* Journ. Amer. Chem. Socy. 1901—96.

fatty acids). So that, varying with the proportions of these salts must soap solution be added before a permanent lather appears.

The *total hardness* of a water is expressed by the number of cubic centimeters of a standard soap solution required to precipitate the earthy salts of one gallon. On boiling a water the calcium, magnesium, and ferrous bicarbonates decompose; the mono-carbonates precipitate and no longer react with the soap solution. The volume of soap solution required for a gallon of the water *after* boiling expresses the *permanent hardness*, that due to earthy sulfates, chlorides, etc. The difference between the total and permanent is called the *temporary hardness*.

The soap solution is made up by dissolving a pure neutral alkali-fatty-acid soap in weak alcohol. It is standarized against a solution of calcium chloride (made by dissolving a weighed quantity of calcium carbonate in hydrochloric acid, evaporating to dryness, and redissolving in water). The soap solution is then diluted until one cubic centimeter exactly corresponds to one milligram of calcium carbonate. Nelson prepares the soap solution by neutralizing pure palmitic acid by normal sodium hydrate; the number of cubic centimeters of the normal alkali solution required times .050035 is the grams of calcium carbonate equivalent to the weight of the palmitic acid taken.

The titration is done on 70 cubic centimeters of the water at 15° Cent. by a soap solution of which one cubic centimeter is equivalent to one milligram of calcium carbonate. This is tantamount to operating on one English gallon (70,000 grains) with a solution of the strength equaling one grain of calcium carbonate per cubic centimeter; if the result is to be expressed in grains per United States gallon, the quantity for the soap test is 58.3 cubic centimeters. The sample is measured into a stoppered flask and the soap solution run in, one cubic centimeter at a time, shaking after each addition until the foam remains permanent for five minutes. One Cc. is deducted for the amount required to produce a lather in distilled water; the remainder is reported as "degrees of total hardness." The standardization is done in the same manner.

Calcium bicarbonate produces an immediate precipitation, but the reaction with magnesium bicarbonate is slower, and one part of magnesium bicarbonate is said to consume as much soap as 1.5 parts of calcium bicarbonate. If for a water containing principally calcium compounds more than 16 Cc. of the titrand is required, or more than 7 Cc. for one containing a considerable proportion of magnesium compounds, another test is made on the water diluted with distilled water, since the precipitate interferes with the exhibition of the end-point.

Another portion of the water is boiled for some time, cooled and titrated as before; the result is the permanent hardness, and the temporary hardness is found by difference.

The permanent hardness is determined by Hehner* by evaporating to dryness 100 Cc. of the water with a measured volume (a) of fiftieth-normal sodium carbonate, a quantity in excess of that required to react with the calcium and magnesium salts other than bicarbonates. The residue is lixiviated by water and filtered; there passes into solution the excess of sodium carbonate which is then determined by titration by N/50 hydrochloric acid, requiring b Cc. The difference between a and b is termed the permanent hardness per 100,000 parts of water.

(Were distilled water subjected to this process, a would equal b and the permanent hardness would be zero. In the case of a natural water there are

* Chem. News, 1898—1—185; Journ. Amer. Chem. Socy. 1899—359.

contained usually calcium and magnesium bicarbonates, calcium sulfate, and sometimes calcium and magnesium chlorides; the bicarbonates, which give the temporary hardness, do not react with the sodium carbonate and on evaporation pass to the monocarbonates, which being insoluble in water, are left as a residue in the lixiviation. But the calcium and magnesium chlorides and sulfates react with sodium carbonate to form calcium and magnesium carbonates and sodium sulfate and chloride; the carbonates remain insoluble in the lixiviation, and the sodium compounds are neutral to hydrochloric acid; hence according to the quantity of sodium carbonate reacting, b is decreased and consequently $a - b$ is increased.)

The total alkalinity of a water is found by directly titrating 100 Cc. by N/50 sulfuric acid, using for an indicator either lacmoid, carminic acid, or azoresorufin. The result is the temporary hardness per 100,000 parts of water provided it contains no sodium carbonate. And if there is no sodium carbonate in the water, the amount of calcium bicarbonate it contains can be calculated from the volume of N/50 sulfuric acid used in the direct titration. But if there be, as is usual, both calcium and magnesium bicarbonates in the water, the result calculated on the former will be inaccurate since the molecular weights of the two compounds differ considerably. However, if the ratio in which the two are present is fairly well known, the calculation can be made accordingly, or the sulfuric acid made proportionally stronger.

In a water that contains sodium carbonate there can be no earthy compounds other than bicarbonates and therefore no permanent hardness; so that in Hehner's process all the original and added sodium carbonate is found in the lixiviation, and $b - a$ is the volume of acid equivalent to the original sodium carbonate. If c represents the total alkalinity as found by direct titration by N/50 acid, then $c - (b - a)$ is the acid corresponding to the earthy bicarbonates, the true temporary hardness.

Calculation. The custom of reporting the results of a water analysis in grains per gallon — English or United States as the case may be — is still retained by many chemists for reasons more or less tenable, but the modern practice of following a decimal system is more in keeping with the scientific trend and should be adopted wherever practicable, with the exception perhaps of 'degrees of hardness.' Since a percentage basis would bring all the figures beyond the decimal point, the results are stated as parts either per hundred thousand or per million of water; gases as cubic centimeters per hundred or per thousand.

It is still a matter of controversy whether the inorganic constituents should be reported as elements, radicals, or compounds. The first two are nearer in harmony with the theory of ionic dissociation in dilute solutions, and relieve the chemist of expressing any opinion as to the debatable matter of the selective union of bases and radicals. But from such a tabulation one is not informed as to whether the water is neutral, or acid or alkaline and to what degree; whether any or much temporary or permanent hardness exists; and whether certain compounds that are believed to be obnoxious for boiler use or manufacturing purposes are present or will separate when the water is concentrated. Nor are the facts that our knowledge of selective association is somewhat vague, and that the conventional combinations can be calculated at any time from the elementary or radical statement, convincing arguments for the adoption of the latter forms.

No absolute rules can be laid down as to the forms of combination that will apply to all waters. The conventional practice is to first combine the alkalies

with chlorine and sulfuric acid; second, the excess of these acids with the earths; and lastly the remainder of the earths with carbon dioxide. Variations from the above and more detailed rules will be found in the works on water analysis. It must be remembered however that certain compounds are incompatible, *e. g.*, an alkali carbonate and calcium sulfate.

B. Analysis of potable water.

1. *Total organic mattter*. A number of processes have been put forward for this determination by Forchammer, Kubel, Woolf, Dittmar and others, but none are quite satisfactory. Two great difficulties are apparent, one that in the organic matter of a water are comprised many bodies of unlike character, the other that their proportion is very minute in potable waters and oxidation during concentration is more than possible.

A. In the procedure commonly called the "moist oxidation process" the organic matter is decomposed by potassium permanganate which converts the carbon and hydrogen into carbon dioxide and water. The action of the oxidizer is always incomplete, however, and with some organic compounds slower and more imperfect than with others; thus, it is said that there is a notable difference in reducing power between fresh animal matter and the same in a putrescent state.

Various modifications of the details of the process have been exploited with a corresponding difference in the oxygen consumed. Wanklyn compounds a liter of water with an excess of standard potassium permanganate solution, makes alkaline with potash, and distills rapidly from a glass retort until 900 Cc. has passed over. The water remaining in the retort, still colored by unreduced permanganate, is acidified by sulfuric acid, mixed with a known volume of standard ferrous sulfate, and the excess of the latter determined by titration with permanganate. The strength of the permanganate is such that one Cc. contains one milligram of available oxygen. The weight of oxygen consumed by the organic matter is readily calculated. Should the water contain ferrous compounds, nitrites, hydrogen sulfide, or other reducers, the result must be corrected therefor.

Another method, wherein the oxidation takes place in an acid solution, is to prepare a permanganate solution of which one Cc. contains .0001 gram of available oxygen, and a solution of oxalic acid of equivalent strength. To 200 Cc. of the water is added 10 Cc. of dilute sulfuric acid and enough permanganate to produce a persistent red color. The mixture is boiled for 15 minutes, then reduced by an excess of oxalic acid solution, and the remainder of the latter titrated back by permanganate. The sum of the volumes of permanganate less that of the oxalic acid is the permanganate reduced by the organic matter.

In another modification, two determinations are made at 80° Fahr., one digested for 15 minutes, in which period it is assumed that reducing compounds are oxidized but not organic matter; the other for four hours to oxidize both. The excess of permanganate is determined by treatment with potassium iodide solution — $K_2Mn_2O_8 + 10KI = 5I_2 + 6K_2O + 2MnO$ — and the liberated iodine titrated by sodium thiosulfate and starch-paste.

In the method of Degener and Maercker the carbon is determined by oxidizing with chromic and sulfuric acids and absorbing the carbon dioxide in a potash bulb as in an ordinary moist combustion. Hertzfield improves the process by interposing a tube containing metallic antimony which serves to retain any chlorine liberated from the chlorides of the water. Burghardt determines the chromic acid reduced by the organic matter by a back titration with ferrous sulfate.

It was found by Barnes that the ratio of oxygen consumed in the permanganate and bichromate oxidations is distinctly higher for waters containing vegetable matter than for those polluted by sewage, independent of the amount of organic matter contained.

B. Flack's scheme for measuring organic matter by the reduction of silver sulfate to metallic silver has not come into general use.

C. In Frankland's process for organic carbon and nitrogen, one liter or more of the water is evaporated to dryness after acidification with sulfurous acid to destroy oxidizing matters. The evaporation is done in a glass dish carefully protected from dust and ammonia fumes. The residue is scraped from the dish, mixed with copper oxide, and burned in vacuo in a glass combustion tube. The products are carbon dioxide, nitrogen and nitric oxide, and are transferred to a gas-measuring tube and the proportion of each determined by the usual gasometric methods. The carbon and nitrogen in the gases are calculated from the usual formulae.

The method requires complex apparatus and careful manipulation. As to the relative merits of the Frankland and Wanklyn processes there has been much discussion, not always confined to scientific arguments. But it is now conceded that both are but empirical and cannot give "more than an approximation to the quantity of certain substances, the presence of which is only circumstantial evidence of the character of the water."

2. *Oxygen*. In water saturated with air the dissolved oxygen is a sensibly constant quantity at a given temperature and pressure. If the water is stored in a closed vessel and remains at a uniform temperature there will be neither a loss or gain of the gas provided the water be pure, but if it contains aerobia the oxygen will steadily diminish. Dupré adopts the number 100 as a standard signifying the quantity of dissolved oxygen in water saturated at 20° Cent.

The determination is made in one of two ways, although methods of the first class are no longer in use, having been supplanted by the simpler volumetric methods of the second: (1) the oxygen, with other dissolved gases, is expelled by heating the water in vacuo, and the gases transferred to a eudiometer for gasometric analysis; (2) the oxidizing action is measured by a standard solution of a reducer, either directly or by a reverse titration. It is essential that no air comes in contact with water during the operation, and that there be no loss through diffusion.

(A.) In the method of Schuetzenberger the water is titrated by a standard solution of the powerful reducer sodium hyposulfite (Na_2SO_3); the indicator is indigotin sulfate which is blue or colorless respectively when oxygen or hyposulfite is in excess. The process, somewhat modified, is to prepare the indicator by adding a little indigo solution to water, then just decolorizing by hyposulfite. Ten cubic centimeters of the hyposulfite solution is run in, followed by the water under examination delivered from a burette, until the liquid becomes blue, then again decolorized by hyposulfite. The hyposulfite is standardized against fully aerated distilled water of which the amount of oxygen in solution is a constant under a given temperature and pressure. Free acids and alkalies disturb the normal conduct of the process.

During the mixing and titration, contact with the air must be prevented. This is accomplished: (1) by arranging that these operations take place in a bottle through which passes a current of a non-oxidizing nearly insoluble gas, *i. e.*, hydrogen. But it has been shown that dissolved oxygen rapidly diffuses from water into hydrogen gas; this difficulty is overcome by running the water into a measured volume of the reducing solution by way of a burette whose embouchure is beneath the surface of the solution, the oxygen being fixed before

it can come into contact with the hydrogen; (2) a simpler plan is that of Blarez, who blankets the water with a layer of purified hydrocarbon oil, and in adding the reagents takes care that the orifices of the delivering vessels dip below the layer. The titration is made in a separatory funnel closed by a cork holding the taps of one or more burettes. The funnel is party filled with mercury, then completely filled with the water. As the reducer is run in, the tap of the funnel is opened to allow a corresponding volume of mercury to escape. The heavy mercury allows a thorough mixing of the water and reducer on shaking the funnel.

(B.) In the method of Mohr the water is shaken up with recently precipitated ferrous hydrate which is perduced to ferric hydrate by absorption of oxygen — $2Fe(OH)_2 + O + H_2O = Fe_2(OH)_6$. The water is made alkaline by sodium hydrate, and a measured volume of standard ferrous sulfate run in; after thorough agitation, the hydrates are dissolved by acidulation with dilute sulfuric acid, and the ferrous sulfate titrated by permanganate. A correction for nitrates present is made by titrating another portion of the water by ferrous sulfate and permanganate after acidification by sulfuric acid.

Letts and Blake fill a globe-shaped separatory funnel completely with the water; a small fraction of the water is withdrawn, and a slightly less volume of strong solution of ferrous sulfate run in through the stem. The globe is then filled up with concentrated ammonia. After stoppering and agitating, the globe is let stand for 15 minutes. It is then reversed, the stem filled with concentrated sulfuric acid, the stopcock opened, and the sulfuric acid allowed to diffuse through the liquid. When the iron hydrates have dissolved, the liquid is drawn out and titrated by permanganate or bichromate.

(C.) Winkler's* method is similar to Mohr's. Manganous hydrate is precipitated from a solution of manganous chloride by potassium hydrate, but if the solution holds dissolved oxygen, a corresponding amount of the precipitate becomes manganic hydrate, thus —

$2MnCl_2 + 4KOH = 2MnO.H_2O$ (manganous hydrate) $+ 4KCl$; and
$2MnCl_2 + 4KOH + O = Mn_2O_3.H_2O$(manganic hydrate) $+ 4KCl + H_2O$.

Manganic hydrate when treated with potassium iodide and an acid dissolves to manganous chloride, liberating iodine —

$Mn_2O_3H_2O + 2KI + 6HCl = 2MnCl_2 + I_2 + 2KCl + 4H_2O$.

Two atoms of iodine correspond to one atom of oxygen in the water.

The determination is made in a cylinder nearly filled with the water; by long pipettes are introduced one cubic centimeter each of potassium iodide and potassium hydrate solutions. The cylinder is stoppered and agitated. Hydrochloric acid is then introduced to dissolve the manganese hydrates, and the liberated iodine is at once titrated by sodium thiosulfate and starch. Nitrites also liberate iodine and must be corrected for, and large amounts of organic matter tend to retain iodine.

(D.) Thresh's iodimetric method.† Oxygen in presence of a carrier, such as nitrogen dioxide, liberates iodine quantitatively from an iodide. The water is mixed with potassium iodide and a weighed quantity of pure sodium nitrite, and acidified by sulfuric acid. First the nitrite reacts with the potassium iodide and sulfuric acid —

$$2KI + 2KNO_2 + 2H_2SO_4 = I_2 + 2K_2SO_4 + N_2O_2 + 2H_2O;$$

then the oxygen of the water reacts with the excess of the iodide —

$$2KI + O + H_2SO_4 = I_2 + K_2SO_4 + H_2O.$$

* Berichte, 1888—2843.
† Journ. Chem. Socy. 1890—185.

All the operations are conducted under a current of coal-gas. The iodine found by the titration with thiosulfate includes *a* that liberated by the oxygen of the water, plus *b* that liberated by a part of the oxygen dissolved in the thiosulfate solution, plus *c*, that formed by the reaction between the iodide and sodium nitrite. Corrections are made for *c* by a blank titration of potassium iodide plus sodium nitrite plus sulfuric acid dissolved in air-free water; and for *b* by a titration of ordinary distilled water, on the assumption that thiosulfate solution and water absorb equal amounts of oxygen.

(E.) Lissonier titrates the water made slightly alkaline, directly with a standard solution of ferrous tartrate, using for an indicator pheno-safranine (a red dye—para-amidophenyl-para-amidophenazonium chloride) which is decolorized by a ferrous salt.

8. *Ammonia.* The nitrogenous organic matter in a water is a complex mixture of a group of bodies more or less easily decomposable and that pass by successive stages to ammonia, nitrous acid, and nitric acid. For these three products fairly accurate methods of determination are known.

(1) Free or already-formed ammonia. The determination of this body, it being in so small a proportion in potable waters, cannot be made by the ordinary gravimetric or volumetric methods. The well known colorimetric scheme due to Nessler is sufficiently delicate. It depends on the yellow to brown hue produced by traces of ammonia in an extremely dilute colorless alkaline solution of potassium mercuric chloride. The formula of Nessler's solution prescribed by Wanklyn is to add to a solution of 35 grams of potassium iodide and 13 grams of mercuric chloride in 800 Cc. of hot water, a cold saturated solution of the latter salt until but little mercuric iodide remains undissolved; then 160 grams of potassium hydrate, and water to the volume of one liter. Finally a little mercuric chloride is added and the mixture allowed to settle until clear and of a light yellow tint.

In this process water entirely free from ammonia is required for dilution. The traces present in ordinary distilled water pass off on evaporating to half its bulk or less, so that on rendering the water slightly alkaline and distilling until the distillate shows no indication of ammonia, a further quantity distilled is praccally pure. A simpler method is to redistill ordinary distilled water after addition of a little sulfuric acid; the acid retains the ammonia already formed or nascent. And if the sample of water is to be filtered before making the test, the filter paper must be purified before use by copious washing with ammonia-free water.

In making the test, the solution containing ammonia or an ammonium salt is poured into a flat-bottomed test-tube (Nessler's tube) of clear glass marked at 50 Cc. Two Cc. of the Nessler's solution is added and mixed by stirring, and the brown color shortly develops.

At the same time a comparison test is made in the same manner on ammonia-free water plus a measured volume of standard solution of ammonium chloride. The tubes are held at an angle over a white porcelain plate. On looking down through them it is seen whether the tints are identical; if so, the weight of the ammonia in the volume of the standard solution of ammonium chloride employed is the weight of ammonia in the water; but if they differ, as is nearly always the case, other tints for comparison are made up with greater or less volumes of the ammonium chloride solution as indicated, until an agreement is had. With practice this can be done quite rapidly. Various colorimeters have been recommended for the comparison. In all cases the temperature of the solutions and the order of the mixture with the reagent should be the same.

The details of the determination in a water as practiced by different chemists vary considerably; one plan is as follows: Two hundred Cc. of distilled water, made slightly alkaline by sodium carbonate, is placed in a large glass retort connected to a condenser by cork fittings. One hundred Cc. is distilled and rejected as containing the ammonia from the water and that adhering to the interior of the apparatus. To the residual water in the retort is added 500 Cc. of the water for analysis and distilled at the rate of about 50 Cc. in 15 minutes. The distillate is received in the Nessler's tubes, 50 Cc. in each, and the first four Nesslerized. Distributed through these is practically all the ammonia in the water, though unequally, the first tube containing approximately three-fourths of all, the fourth practically none. The sum of the ammonia in the four is set down as the free ammonia in 500 Cc. of the water.

2. *Albumenoid ammonia.* Wanklyn's method. On digesting water containing albuminous matter with an alkaline solution of potassium permanganate, the nitrogen is converted into ammonia, more or less completely according to the nature of the bodies and the conditions of the experiment. It is said that by repeated distillations all the nitrogen may be so converted, but certain bodies, like urea, evolve ammonia steadily and continuously for a long time.

The method is practically the same as that for free ammonia with the exception that a strongly alkaline permanganate solution is mixed with the water; the ammonia determined in the distillates is here the sum of the free and albumenoid; deducting the former, found by a previous test, gives the latter. But as the process involves not merely a distillation of free ammonia as in (1), but also a chemical decomposition of the organic matter, and as this decomposition is never instantaneous and often very slow, the question arises how far to proceed with the distillation before considering it practically complete. The proposal to stop the distillation when the last fraction contains not more than one per cent of the entire ammonia of the distillate would seem to be an ample allowance.

3. *Nitrogen* by Kjeldahl's method. Recently this process has been applied with success to the determination of total nitrogen in water. Five hundred Cc. of the water is mixed with ten Cc. of concentrated sulfuric acid and evaporated until the acid becomes concentrated, clear and nearly colorless, when a little permanganate may be added. The residue is diluted, made alkaline by sodium hydrate, and either filtered and Nesslerized directly, or distilled and the ammonia determined as usual. Leffman and Beam determine free ammonia by mixing 200 Cc. of the water with sodium hydrate and carbonate, filtering through cotton, and Nesslerizing the middle 100 Cc. of the filtrate; then deducting the result from the nitrogen by the above method to obtain the total organic nitrogen. Drown and Martin boil 500 Cc. of the water to 800 Cc. to expel free ammonia previous to the Kjeldahl determination.

4. *Nitrates.* The methods of Schulze, Lunge, Trommsdorf, etc., ordinarily adopted for the determination of nitrates, are most suitable for moderately large amounts and can only be used for potable waters after concentration of a large volume; as this is objectionable on account of the liability of oxidation of nitrites and for other reasons, they are seldom used.

(1) Sprengel's method. When nitric acid is brought in contact with (colorless) phenolsulfuric acid there is formed picric acid —

$$C_6H_4.OH.SO_3H + 3HNO_3 = C_6H_2OH(NO_2)_3 + 2H_2O + H_2SO_4.$$

On adding an excess of ammonia, the highly tinctorial yellow ammonium picrate is formed.

Phenolsulfuric acid of a definite composition is prepared, according to Johnson, by digesting for eight hours on the water bath, a mixture of four parts of

crystallized phenol with ten parts of concentrated sulfuric acid. After cooling there is added three volumes of water and one volume of concentrated hydrochloric acid — the latter heightening the delicacy of the reaction.

The process is to evaporate to dryness on the water bath in small porcelain dishes ten Cc. of the water and the same volume of a standard solution of potassium nitrate. The accuracy is said to be increased if a little sodium carbonate be added to prevent loss of nitric acid. The residues are stirred up with one Cc. of the reagent. Where large amounts of nitrate are in the water the solution quickly assumes a red color, in good potable water not for ten minutes. After standing for 15 minutes, the solutions are washed into measuring jars and after adding a slight excess of ammonia, diluted to 100 Cc. The yellow liquids are compared colorimetrically, and another test made with a standard approximating the concentration of the water.

Chlorides interfere with the reaction and are to be removed by silver sulfate; or the standard may have a corresponding addition of sodium chloride — sulfates have no effect. Should the water be yellow originally it is decolorized by aluminum hydrate and filtered.

(2) The Indigo process. Sulfindigotic acid is decolorized by free nitrous and nitric acids, not however in strict molecular proportion. The sulfindigotic acid is made by digesting indigotin in fuming sulfuric acid, the solution diluted somewhat and the strength determined by a test with potassium nitrate, then further diluted until one Cc. is bleached by approximately one Cc. of N/100 potassium nitrate solution.

The process is tentative and rather tedious, and requires close attention to details. To 20 Cc. of the water in a small flask is added a measured volume of the indigo solution, as much as it is thought will be decolorized, then a volume of concentrated sulfuric acid equal to that in the flask. On heating for five minutes in the water bath either the solution is completely decolorized or remains blue. The test is repeated with greater or smaller amounts of indigo solution until the equivalent is arrived at — that is, when the liquid remains but faintly blue. Then it is ascertained what volume of standard potassium nitrate solution will produce the same tint with the same volume of indigo solution operating under the same conditions as before.

(3) Mueller's method. Diphenylamin in concentrated sulfuric acid gives a blue coloration with nitric acid. Into a small test-tube is poured 5 Cc. of a solution of the reagent (.200 gram in a liter of concentrated sulfuric acid) and one Cc. of the water. Shortly a blue color is developed. Comparison tests are made with solutions of potassium nitrate ranging from one-half to five milligrams of nitric acid per liter. If nitrous acid is present in the water it may be oxidized to nitric by potassium permanganate and both read as nitric.

(4) Hooker's method. A solution of carbazol (diphenylimid, $C_6H_4.NH.C_6H_4$) in sulfuric acid yields a green color with nitric acid. One hundred Cc. of the water is treated with sufficient silver sulfate to precipitate the chlorine from the chlorides of the water, together with some aluminum sulfate, which is decomposed by the carbonates of the water with precipitation of aluminum hydrate which assists in filtration. The liquid is made up to a volume of 110 Cc. and filtered; to two Cc. of the filtrate is added double the volume of concentrated sulfuric acid and the mixture cooled, then one Cc. of a .04 per cent solution of carbazol in concentrated sulfuric acid. In a few minutes a bright green color appears. The standards are the same as in (3).

(5) Reduction to ammonia. Nascent hydrogen reduces nitrous and nitric acids to ammonia —

$$NaNO_3 + 2H = NaNO_2 + H_2O; \text{ and } NaNO_2 + 6H = NH_3 + NaOH + H_2O.$$

For the generation of hydrogen in the water various metals and combinations of metals have been proposed; iron and zinc in acid solution, and sodium-amalgam, aluminum, copper-zinc, and aluminum-copper-zinc alloy in alkaline solution. The copper-zinc couple is composed of a sheet of zinc coated with spongy copper, made by immersing the zinc in a solution of cupric sulfate. Aluminum has largely taken the the place of other metals as it is quite as efficient as any, convenient, and readily obtained pure. The reaction is $Al_2 + 6NaOH = 3Na_2O.Al_2O_3 + 6H$.

With 50 Cc. of the water is compounded a little sodium hydrate solution (made from sodium and distilled water), and a strip of aluminum foil immersed in the liquid. After standing for from 18 to 24 hours a portion of the liquid is withdrawn, and from 1 to 25 Cc., according to the amount of ammonia, Nesslerized. If clear and colorless it is unnecessary to distill the ammonia and the test is applied direct after dilution with water (free from carbonic acid which might precipitate aluminum hydrate). A correction is made for nitrous acid. Some ammonia is carried off mechanically by gaseous hydrogen; if the container is a flask fitted with a guard tube of dilute hydrochloric acid the ammonia may be caught and Nesslerized; Hazen instead makes a correction based on the theoretical amount carried off. The results by this method as compared with the phenolsulfuric method are lower according to Gill, higher according to Hazen and Clark.

5. *Nitrites.* The methods for nitrous acid are all colorimetric, that of titration to nitrate with potassium permanganate being seldom available on account of the minute proportion of the nitrite to be determined, and the organic matter accompanying it.

(1) Method of Griess.* Para-amidobenzene-sulfonic acid (sulfanilic acid, $C_6H_4.NH_2.HSO_3$) with alpha-amido-napthalin-acetate (or napthylamine, $C_{10}H_7.NH_2$) in acetic solution produce with nitrous acid the compound amid-alpha-napthyl-azobenzene-sulfonic acid, coloring the liquid pink to red—

$$C_{10}H_7.NH_2 + C_6H_4.NH_2.HSO_3 + HNO_2 = C_{10}H_6(NH_2).N_2.C_6H_4.HSO_3 + 2H_2O.$$

Two Cc. of solutions of each of the above reagents are added to 25 Cc. of the water held in a graduated cylinder. One Cc. or more of a standard solution of sodium nitrite (made from silver nitrite and sodium chloride) is made up with pure water to 25 Cc. and the same quantities of reagents added. The comparison of the colors may at first be done by dilution, but finally by adjusting the concentration of the standard as regards nitrous acid to approximately equal that of the sample of water.

Green and Evershed † prefer anilin hydrochloride to sulfanilic acid as the color is more rapidly developed. Griess has also proposed metaphenylene-diamin which with nitrous acid forms triamido-benzene (Bismark brown, $NH_2.C_6H_4.N : N.C_6H_3(NH_2)_2$).

(2) Trommsdorf's method is based on the liberation of iodine from zinc oxide by nitrous acid—$ZnI_2 + 2NaNO_2 + 2H_2SO_4 = I_2 + N_2O_2 + Na_2SO_4 + ZnSO_4 + 2H_2O$. In presence of starch-paste the liquid becomes blue in proportion to the iodine liberated.

To 100 Cc. of the water is added 3 Cc. of a solution containing zinc iodide and starch paste, then one Cc. of dilute sulfuric acid. Into four cylinders are placed for comparison 100 Cc. of distilled water with one to four Cc. of standard sodium nitrite and one Cc. of dilute sulfuric acid. Thresh substitutes potassium iodide for the zinc compound, and previous to the test, shakes up the water with air to insure saturation with oxygen. He states that the time,

* Berichte, 21—1830.

† Chem. News 1892—1—109.

temperature, quantities of potassium iodide and starch, and oxygen held by the water must be constant, when the depth of color and rapidity of its formation are proportional to the nitrous acid.

According to Musset, bacteria give a blue color with zinc-starch-iodide and acetic acid, hence the water is to be acidified by sulfuric acid and distilled, and the nitrous acid determined in the distillate. Proskauer removes bacteria by filtering through a thick washed filter paper.

6. *Bacteria.* Supplementing the chemical examination, a bacteriological test is valuable, at least as confirmatory evidence of the quality of a water. Many chemists consider that a positive opinion as to the quality can only be formed from a consideration of the source of the water and its environments, the chemical composition, and the bacteriological condition; yet others do not attach so much importance to the last named as to the two former.*

A test can be made by introducing a drop of the water into a medium of sterilized gelatin, and after a certain period, examining the culture for pathogenic germs. A bouillon culture may be injected into the abdominal cavity of a small animal, observing if disorders or death follows the inoculation. Directions for enumerating, recognizing and differentiating the various species will be found in works on bacteriology.

Standards. For boiler use any considerable proportion of inorganic matter, especially of calcium and magnesium compounds, is detrimental, while a moderate quantity of organic matter is of no consequence. Scale is formed by the deposition of suspended particles, the dehydration of soluble silicic acid, the decomposition of calcium and magnesium bicarbonates, and the crystallization of calcium sulfate. Soluble salts above a certain proportion are liable to cause the water in a boiler to foam at temperatures above 100°.

Free sulfuric acid above five parts per hundred thousand of water causes corrosion of the boiler shell, and it is said that magnesium chloride and sulfate are especially objectionable on this score on the assumption that the ordinary temperature and pressure of the water in a boiler are together sufficient to dissociate these compounds with liberation of hydrochloric and surfuric acids (e g., $MgCl_2 + H_2O = MgO + 2HCl$), yet do not suspend the action of the free acids on iron.

In pronouncing on the quality of a water for boiler purposes, the standards of excellence will differ considerably according to the locality in which the water is found. The supplies in many regions through the Western States are almost exclusively of a quality that would be condemned nearer the coast, and in the table below, five or ten grains may be added to the figures there given. The "incrusting solids" include whatever is precipitated by the concentration of the water (the evaporation never extends to dryness) in the boiler, namely suspended matter, silica, carbonates of calcium and magnesium, and calcium sulfate; some would include the magnesia from the sulfate and chloride. All of the other inorganic compounds are grouped as "non-incrusting" or "foam-causing".

The following conventional table is applicable to the ordinary waters of the Eastern and Central States. The quantities are in grains per U. S. gallon.

Quality.	Incrusting.	Non-incrusting.
Good	Below 10	Below 10
Fair to passable	10 to 20	10 to 15
Poor	20 to 40	15 to 35
Very poor	40 to 60	35 to 50
Unfit for use	Above 60	Above 50

* Chem. News, 1893—2—207.

For manufacturing purposes in general the most harmful impurities are free acids (drainage from factories) large amounts of total solids, especially if hard toward soap, and organic matter. Special products, that depend for their value on qualities of taste, odor, color, clearness, etc., require water free from whatever would modify or impair them.

The wholesomeness of a drinking water is not compromised by a moderate amount of earthy and alkali compounds nor organic matter. But aside from the natural aversion to the use of water containing vegetable or animal refuse there remains the fact that organic matter especially if putrescent, is an excellent medium for the growth of pathogens and it is conceded that unwholesome water is responsible for the origin and spread of certain diseases. Free ammonia, nitrous and nitric acids, albuminous bodies and chlorine are indications of sewage contamination, and their presence above certain minimum amounts, intelligently interpreted, lead the chemist to condemn a water on sanitary grounds. The subject is too extensive to be considered at length in this place; reference may be had to the recent works on water analysis.

No absolute standard can be laid down to which a drinking water must conform to be considered wholesome, and no single analysis is a sufficient warrant for passing judgment where the sources of the supply are subject to modification periodically or irregularly. There must be considered the geological strata permeated by the feeders, the size and character of the well or reservoir, and in surface waters, the area of the water-shed and whether thickly or sparsely populated, the contiguity of drains and sewers, and any special conditions that might allow temporary or permanent contamination. A well or stream may receive organic impurities from drainage of the soil in populated districts or by infiltration of sewage, storm water carrying in surface filth, roots of trees reaching a well, dripping back from pumps, and dust and leaves blown in.

The color, odor and reaction, and an examination of the sediment deposited on standing may give valuable hints as to the past or present condition.

In general a potable water may be considered passable when the following limits per 100000 parts of water are not exceeded.

(1) Residue from evaporation, 50 parts; but this amount of inorganic solids is often exceeded in undoubtedly wholesome waters. The less the amount of organic matter of any kind in the residue, the safer the water.

(2) Sodium chloride, one part; the source of the water always to be considered.

(3) Free ammonia, .005 part, and albumenoid ammonia, .015 part.

(4) Of potassium permanganate consumed, one part. Wanklyn states that a water of first-class purity does not consume more than .0005 gram oxygen per liter; average drinking water, .002 to .003; and dirty water, considerably more than .003.

(5) Nitric acid, .05 part, and nitrous acid .0005 part.

(6) Iron, lead, or copper, .2 part.

In drawing a conclusion the above limits are to be viewed in their interrelation as well as separately. Wigner adopts a scale of purity, allowing one unit for a certain amount of each impurity, which he claims can be applied to every potable water.

FERTILIZERS.

Commercial fertilizers may be manures, vegetable matter or its ashes, animal or fish refuse, the waste products of manufactories, minerals in their natural state or after chemical treatment, or naturally occurring salts. The most valuable ingredients of a fertilizer are nitrogen, potash and phosphoric acid, though other bodies are esteemed for certain conditions of soil and plant. In the valuation of a sample the state of combination of these bodies is of importance for the reason that plants can more readily assimilate some combinations than others.

In regard to analytical processes fertilizers may be divided into three groups: (1), organic material, containing more or less inorganic; (2), phosphates, natural or chemically altered; and (3), alkali salts. The preliminary treatment and the course of analysis differ to some extent.

The organic matter in a fertilizer is invariably destroyed previous to the determination of the inorganic constituents. If done by ignition in air the heat must be kept under control lest it become so high as to volatilize some alkali chloride; many simply char the sample, then lixiviate the soluble alkali salts, burn the remainder to an ash, return the solution, and evaporate to dryness. Saturation of the sample with sulfuric acid before ignition facilitates the combustion, and at the same time allows a higher heat since alkali sulfates are less volatile than chlorides. Instead of calcination, the organic matter may be oxidized by boiling with aqua regia, fuming nitric acid, nitric acid with sodium chlorate, or other strong oxidizer.

While the determination of phosphoric acid in a phosphate or superphosphate presents no great difficulties, yet it so complicates the determination of the bases that its previous removal is always to be advised unless the operator has had an extended experience in the analysis of bodies of this nature.

Mineral salts, such as ammonium sulfate, are analyzed by the usual methods for commercial salts in a more or less pure condition, and need no special mention.

PHOSPHORIC ACID.

In the manufacture of the commercial product known as 'superphosphate', tri-calcic phosphate, $Ca_3(PO_4)_2$, is treated with sulfuric acid. The proportion of acid to phosphate determines the composition of the resulting product, thus —

$$Ca_3(PO_4)_2 + H_2SO_4 = Ca_2H_2(PO_4)_2 \text{ (dicalcic phosphate)} + CaSO_4.$$
$$Ca_3(PO_4)_2 + 2H_2SO_4 = CaH_4(PO_4)_2 \text{ (monocalcic phosphate)} + 2CaSO_4.$$
$$Ca_3(PO_4)_2 + 3H_2SO_4 = 2H_3PO_4 \text{ (phosphoric acid)} + 3CaSO_4.$$

The product is of value to the agriculturist in proportion as it is soluble in water. But the monocalcic phosphate suffers by age a peculiar retrogression or reversion, gradually passing to a form insoluble in water though soluble in weak acids. The reversion is said to be due principally to a reaction between monocalcic and tri-calcic phosphates — $CaH_4(PO_4)_2 + Ca_3(PO_4)_2 = 2Ca_2H_2(PO_4)_2$ (dicalcic phosphate). A gradual evolution of hydrofluoric acid in mineral phosphates containing fluorine is said also to cause reversion.

We may therefore in a commercial superphosphate distinguish three combinations of calcium with phosphoric acid, viz.

1. That soluble in cold water; either free phosphoric acid or monocalcium phosphate, also acid magnesium phosphate. This form is the most valuable as a fertilizer.

2. That insoluble in water but soluble in solutions of certain salts and in weak acids; dicalcium phosphate, also iron and aluminum phosphates. It is generally considered of somewhat less value than that of (1), but much more so than that of (3).

3. That insoluble in water and weak acids but soluble in strong acids; tricalcium phosphate.

Total phosphoric acid. The sample is dissolved in a mineral acid that may be hydrochloric, nitric or sulfuric. When organic matter is in the sample some oxidizer is added to the acid to destroy it, or it may be burned by a previous ignition in the air provided there is no organic phosphorus present. The solution is diluted with water to a definite volume, and an aliquot part, containing a convenient weight of phosphoric acid, filtered for the determination.

A number of methods have been proposed of which some have become obsolete on account of their complexity, though yielding correct results. The best known are as follows:

1. Phosphoric acid forms insoluble compounds with lead, silver, stannic tin, ferric iron, and mercuric mercury. Silver phosphate precipitates only from a neutral solution that may be secured by nearly neutralizing the solution by an alkali and stirring in silver carbonate. Stannic phosphate is formed when metallic tin is oxidized by hot concentrated nitric acid containing phosphoric acid. Ferric phosphate is carried down, associated with basic ferric acetate, when the solution of the phosphate is mixed with ferric chloride and precipitated hot by an alkali acetate. Although these methods afford a good separation of phosphoric acid from calcium they are not much in use for fertilizer analysis.

2. The citric acid method. When an acid solution of phosphates of calcium, magnesium, iron, aluminum, etc., is made alkaline by ammonia there forms a precipitate which is a mixture of the phosphates of the various bases. But if previous to the addition of ammonia there be added enough of a magnesium salt to combine with all of the phosphoric acid, and enough citric or tartaric acid to form citrates or tartrates of the other bases, then on supersaturation by ammonia there is precipitated only ammonium magnesium phosphate.

The acid solution of the phosphate is mixed with a sufficiency of magnesic citrate, then with a large excess of ammonia, and allowed to stand for several hours. The precipitate is filtered, washed with dilute ammonia, and ignited to the pyrophosphate $Mg_2P_2O_7$; if necessary, the pyrophosphate may be dissolved in acid and any residue of silica filtered and weighed and the weight deducted.

A volumetric determination of the precipitate may take the place of ignition and weighing. It is dissolved in an excess of standard acid and titrated back by standard alkali.

The results of the citrate method are fairly accurate, the gain due to the coprecipitation of the phosphates of other bases of higher molecular weight than magnesium being compensated to some degree by the solubility of the precipitate in the citrate solution. It is said that for each base the magnesium in the solution must bear a certain ratio to the citric acid. According to Neubauer, on igniting magnesium pyrophosphate there is a loss by volatilization of phosphoric acid ranging from .6 to 3 per cent or more of the pyrophosphate, according to its weight, and the result should be corrected accordingly.

3. The Molybdate method. Here the phosphoric acid is precipitated as ammonic phosphomolybdate from an acid solution. The free acid should be nitric in all cases; a hydrochloric solution is evaporated to a small bulk after addition of concentrated nitric, when the remaining chlorine will not be in quantity great enough to interfere with the precipitation; a sulfuric solution is nearly neutralized by ammonia, and ammonium nitrate added.

On the addition of a solution of molybdic acid in nitric acid and ammonium nitrate there forms a granular yellow precipitate, slowly if allowed to stand without agitation, more rapidly if stirred and heated. After filtering and washing with either the diluted precipitant, a weak solution of ammonic nitrate or sulfate, or simply cold water, the precipitate may be further treated in one of several ways.

A. By direct weight.* A determination made by drying and weighing the yellow precipitate is doubtless quite as accurate as by any volumetric method depending on the invariability of the composition of the precipitate. To insure a definite composition close attention must be paid to the temperature and acidity of the solution and reagent, the time of repose, agitation and other conditions. The precipitate is filtered on a tared paper or through a Gooch crucible, and the washing, or at least the final washing, is done with water. According to most authorities the precipitate approaches the composition of $48MoO_3.2P_2O_5.10NH_3.11H_2O$.

On heating the precipitate to 400 to 500°, it loses ammonia and becomes a molybdenum phosphate, containing 4.018 per cent of phosphoric acid, of almost a black color and not hygroscopic; overheating leaves a gray mass indicating the separation of some molybdic acid.

B. The Molybdate-magnesia method. The yellow precipitate is dissolved in dilute ammonia which decomposes it to ammonium phosphate and ammonium molybdate, both freely soluble. The solution is nearly neutralized by hydrochloric acid and heated until any co-precipitated silica or alumina separates. To the filtrate is added a solution of ammonium magnesium chloride and considerable free ammonia; a crystalline precipitate of ammonic magnesic phosphate falls, which is to be washed with dilute ammonia, ignited, and weighed as magnesium pyrophosphate, $Mg_2P_2O_7$.

C. Pemberton's method is to obtain the phosphate in a nitric acid solution, neutralize the free acid by ammonia, acidify with strong nitric acid, and add ammonium nitrate. The solution is then heated, and an aqueous solution of ammonium molybdate stirred in. The ammonium molybdate immediately decomposes with the free nitric acid to form ammonium nitrate and collodial molybdic acid which remains in solution. The yellow precipitate segregates quickly, and is filtered and washed with water. The filter and precipitate are thrown into a beaker and dissolved in an excess of standard potassium hydrate — $(NH_4)_6(MoO_3)_{24}(PO_4)_2 + 46KOH = (NH_4)_4H_3(PO_4)_2 + (NH_4)_2MoO_4 + 23K_2MoO_4 + 22H_2O$. The excess of potassium hydrate is then titrated back by a standard acid and phenol-phthalein.

D. The yellow precipitate, formed under fixed conditions, may be dissolved in dilute ammonia, acidified by sulfuric acid, the molybdic acid reduced by zinc to a lower oxide, and the latter determined by titration with standard permanganate back to the trioxide (page 340).

E. Jabert determines the ammonia of the yellow precipitate by decomposing the precipitate by potassium hydrate solution and distilling the ammonia into

* Journ. Amer. Chem. Socy. 1896—23.

standard sulfuric acid. The excess of sulfuric acid is found by titration with standard alkali. The relation of ammonia to phosphoric acid in the precipitate is claimed to be more constant than the relation of phosphoric to molybdic acid or to the entire precipitate.

4. The Uranium method. Leconte first proposed that the reaction between uranium and phosphoric acid be utilized as a method for the latter body. When a salt of uranium and phosphoric acid are mixed there is precipitated hydrogen uranyl phosphate, a yellow compound insoluble in water and dilute acids; if an ammonium salt be present in the solution the precipitate is ammonium uranyl phosphate. The relation of uranium to phosphoric acid is the same in both — $Ur_2O_3P_2O_5 + aq$, and $Ur_2O_3.2NH_4O.P_2O_5 + aq$.

A. Gravimetric. The method due to Sutton is available only when there is no iron or aluminum in the phosphate solution. The solution is prepared so as to contain only acetic as a free acid, and precipitated at a boiling heat by uranium acetate. The precipitate, at first slimy, becomes crystalline on washing by decantation with hot water. On drying and ignition it passes to uranium phosphate $UrPO_4$. This process has been superseded by the volumetric one following.

B. Volumetric. The titration of the phosphoric solution is done by a standard solution of uranic nitrate. The end-point is observed by spotting a drop of the titrate with a drop of a freshly prepared solution of potassium ferricyanide, uranium ferricyanide appearing as a chocolate brown coloration. The end-point is not manifested as sharply as could be desired.*

As applied to a superphosphate the solution in hydrochloric acid is first precipitated by magnesic solution, citric acid, and ammonia, thus separating iron and other bases that might interfere in the titration. The washed precipitate is dissolved in dilute nitric acid, nearly neutralized by ammonia, and enough ammonium acetate added that all the free acid may be acetic. The solution is then heated to boiling and titrated by uranium nitrate that has been set against sodium or ammonium phosphate or ammonic magnesic phosphate.

The process is rapid, and fairly accurate when certain precautions have been observed, among which is that the standardization and the titration be done on the same material and under like conditions.

Soluble phosphoric acid. For the determination of the soluble phosphates of a superphosphate a large weight of the sample is treated with cold water. Some direct to lixiviate several times with small quantities of water, others (believing that iron and aluminum phosphates are soluble in a concentrated solution of monocalcium phosphate) treat with a large volume at once. The mixture is filtered through a dry paper and the residue washed with water until the filtrate and washings reach a certain volume; from this an aliquot part is withdrawn for the determination which may be made according to any of the methods outlined for total phosphoric acid.

If there be no other free acid in the sample the amount of free phosphoric acid may be determined volumetrically. Kalman and Messels † state that if a solution of acid calcium phosphate be titrated by caustic alkali and phenolphthalein, too high results will be obtained on the assumption that one molecule of alkali saturates one-half molecule of phosphoric acid; but if now the liquid be filtered and the filtrate titrated back by standard hydrochloric acid and methyl orange, the result of this titration will be as much too low as the

* Crookes, Select Methods, 2d Ed. 524.

† Chem. News, 1895—2—23.

former was too high, and the arithmetical mean of the two will be the correct acidimetric value.

Another method is that of titrating the solution directly by standard potassium hydrate and methyl orange; when the red color disappears there remains monocalcium phosphate. If now there be added to the titrate some calcium chloride, the reaction $CaH_4(PO_4)_2 + 2CaCl_2 = Ca_3(PO_4)_2 + 4HCl$, or $2KH_2PO_4 + 3CaCl_2 = Ca_3(PO_4)_2 + 2KCl + 4HCl$ ensues, and the titration is continued with phenol-phthalein. With methyl orange as indicator one molecule of potassium hydrate neutralizes one molecule of phosphoric acid forming KH_2PO_4, while with phenolphthalein the ratio is as one to one-half.

Reverted phosphoric acid. The determination of this form of phosphate is essentially conventional and should be carried on under conditions sanctioned by the majority of chemists engaged in this line of work.* The problem, as yet not solved with entire satisfaction, is to find some liquid that will extract the reverted phosphate without attacking the insoluble phosphoric compounds. Among the reagents that have been proposed are very dilute solutions of organic acids, ammonium oxalate, ammonium sulfate, etc., but ammonium citrate has been generally adopted. The solution advised by the American Association of Official Agricultural Chemists is strictly neutral and of the specific gravity of 1.09 at 20° Cent. Into 100 cubic centimeters of the citrate solution, heated to 65°, is dropped the filter containing the residue from the water extraction; the flask is stoppered and vigorously shaken, then heated on the water bath to 65° for one-half hour. The solution is filtered and washed with water at 65°.

The citrate solution may be treated in different ways: (1), the phosphoric acid may be determined in an aliquot part; (2), a portion united with a corresponding part of the water solution and the phosphoric acid determined in the mixture; or (3), it may be rejected, and the difference between the total acid of the sample and that of the water-soluble plus insoluble acid called the reverted acid. The reason for the last named course is the belief that the large amount of organic matter such as citric acid would hinder complete precipitation by the usual reagents; it has been found, however, that as regards the molybdate process, citric acid in moderate quantity is without practical effect—probably different kinds of organic matter have an unequal power as regards holding up phosphoric acid.

Ross proposes to destroy the citric acid and other organic matter by evaporating the solution with concentrated sulfuric acid and mercuric oxide, diluting and neutralizing by ammonia, acidifying by nitric acid, and precipitating by molybdate solution.

Insoluble phosphate. The residue from the citrate extraction is ignited to burn organic matter, then dissolved in hydrochloric acid, or at once dissolved in aqua regia, and the phosphoric acid determined in an aliquot part by one of the usual methods.

POTASH.

The only precipitant for potassium in common use is chloroplatinic acid. In favor of this reagent it may be said that it is almost specific for potassium, no other common metal except ammonium forming a precipitate insoluble in water or alcohol; the high combining weight of platinum reduces the effect of mechanical errors; the precipitate is fairly insoluble in dilute alcohol, and easy to filter and wash. Against it is the coarsely crystalline character of the

* Chem. News, 1892—1—209 and 221.

potassium platinchloride, rendering it liable to occlude other compounds, and its decomposition on ignition.

In the usual run of fertilizers there are found more or less calcium, iron, aluminum, magnesium, and other bases, and sulfuric and phosphoric acids. It has been considered the better plan to remove these from the solution before precipitating the potassium, though by the adoption of certain precautionary measures their disturbing influence may be brought to a negligible minimum.

Usually the sample is extracted by water only, as it is considered that all the agriculturally valuable potassium will be withdrawn thereby. The removal of the bases and acids and destruction of organic matter may be done in the entire solution or in the aliquot part withdrawn for the determination. The reagents for precipitation of the bases and acids may be barium chloride with barium hydrate followed by ammonium carbonate and oxalate; barium chloride followed by ammonium carbonate; ammonium oxalate and ammonia; barium oxalate in hydrochloric acid and a little hydrogen peroxide (to peroxidize ferrous salts) followed by ammonia, etc.

The filtrate after one of these separations is evaporated to dryness, best after addition of a little sulfuric acid to convert the potassium salt to the sulfate not volatile at redness. Should the filtrate contain soluble organic matter or ammonium salts, it is generally ignited in the air. The residue is taken up with water, filtered, acidified by hydrochloric acid, and is ready for precipitation.

A moderate excess of chloroplatinic acid is added, and the liquid evaporated to a thick syrup. This is taken up by 80 per cent alcohol, and filtered on a tared paper or a Gooch crucible. The washing is done first by alcohol, then a solution of ammonium chloride saturated with potassium platinchloride (for the purpose of decomposing adhering impurities to soluble compounds), finally by alcohol. The filter and precipitate are dried at 100° to 110° and weighed. After weighing, the filter is replaced in the funnel and washed with hot water; any insoluble impurities remain and may be weighed and deducted.

Other methods of treating the precipitate are to dissolve it in hot water, filter, evaporate to dryness in a small tared platinum dish and weigh; to decompose it by ignition to potassium chloride and platinum, lixiviate the former and weigh the latter; etc.

According to Moore the precipitation may take place in presence of iron, aluminum and other chlorides, purifying the precipitate by washing successively with hydrochloric acid in alcohol, ammonium chloride solution, and 85 per cent alcohol.

Perchloric acid forms with potassium a finely-crystalline powder of potassium perchlorate, $KClO_4$. Although a specific precipitant for potassium, its use is somewhat limited by the necessity of the absence of sulfates. The acid solution of potassium chloride is evaporated to a small bulk, mixed with a moderate excess of perchloric acid solution, more in presence of phosphates, and evaporated to a syrupy consistence. The syrup is diluted with alcohol, filtered on asbestos, washed by decantation, dried at 130° and weighed.*

Phosphomolybdic acid has been proposed as a precipitant, the potassium phosphomolybdate being much less soluble than the corresponding compounds of other bases with the exception of ammonium; it contains about five per cent of its weight of potassium. The reagent is prepared by decomposing ammonium phosphomolybdate by aqua regia which breaks up the ammonium to nitrogen and water. The potassium is obtained as nitrate in a concentrated slightly acid

* Chem. News, 1896—1—17; Journ. Amer. Chem. Socy. 1897—33.

solution and the reagent added. The mixture is evaporated to dryness at not over 50° and taken up by a liquid compounded of a dilute solution of the precipitant plus sodium nitrate and saturated with potassium phosphomolybdate. The liquid is filtered on two balanced papers, washed with the same liquid as was used for solution of the residue, and the papers dried and weighed. The object of the double filter is to neutralize the gain due to the solids in the adhering washing fluid.

NITROGEN.

The nitrogen of a fertilizer may be in one or more of several combinations: (1), as ammonia or a salt of ammonium; (2), as nitrate, rarely as nitrite; (3), as a proteid; (4), as other organic compounds. The nitrogenous fertilizers are dried blood, flesh, fish or animal refuse, guano, oil-cake, barnyard manure, and commercial nitrates or salts of ammonium.

The determination of nitrogen by the absolute, soda-lime, and Kjeldahl methods and modifications follows the usual routine, with a few changes to suit the material in hand. Of the three the Kjeldahl is most in use, the absolute method but seldom.

The nitrogen of an ammonium salt is determined by suspending the sample in a moderately concentrated solution of sodium hydrate and distilling the ammonia into standard sulfuric acid; the excess of acid is titrated back by standard alkali. Should the sample contain also nitrogenous organic matter, for the sodium hydrate is substituted magnesia which has less tendency to decompose the organic matter with formation of ammonia. Ammonium magnesium phosphate is not completely decomposed by distillation with magnesia unless it has previously been dissolved in sulfuric acid.

Nitric acid. The combined nitric acid in a fertilizer may be determined in several ways.

(1). Reduction of the nitrate to nitrogen and measuring its volume.

(2). Reduction of the nitrate to nitric oxide by a reducing agent (*e. g.*, ferrous chloride), and determining either the iron oxidized, the volume of nitric oxide, or the reducing power of the nitric oxide.

(3). Conversion of the nitrate to ammonia and its determination. The reduction may be effected by ignition with soda-lime, boiling with concentrated sulfuric acid, by nascent hydrogen, or electrolytically.

(4). Measuring directly or indirectly the oxidizing power of the nitric acid. There are included various colorimetric methods depending on the formation or destruction of a color of some reagent held in aqueous solution.

The determination by conversion into nitrogen by ignition with cupric oxide, conversion to ammonia by sulfuric acid or soda-lime, and by colorimetric methods have been described elsewhere (pp. 307 and 377).

A. Reduction to nitric oxide. In all determinations by methods on this principle, air must be rigorously excluded since nitric oxide readily combines with oxygen. The operation may be conducted in vacuo, or under hydrogen or carbon dioxide with special precautions to insure the freedom of the gas from traces of air.

In the method of Pelouze the nitrate is boiled in a glass retort with a known volume of a standard solution of ferrous chloride in dilute hydrochloric acid, under a current of hydrogen. The liquid is cooled while the gas still passes, and the iron remaining as ferrous chloride is titrated by standard potassium bichromate; or the ferric chloride formed may be titrated by a standard reducing solution. The weight of nitric acid is calculated from the equation $2HNO_3 + 6FeCl_2 + 6HCl = N_2O_2 + 3Fe_2Cl_6 + 4H_2O$.

Schultze-Tieman. A small flask A, Fig. 175, contains the concentrated solution of the nitrate and is closed by a two-hole stopper. From the stopper pass two long glass tubes bent downward, one, B, dipping into a beaker filled with a solution of ferric chloride in hydrochloric acid, the other, C, bent upward at the orifice to enter the mouth of a gas-measuring tube D filled with a solution of sodium hydrate and standing in a trough E of the same liquid. There are short rubber joints in the tubes B and C that may be closed by a pinch-cock or compression by the fingers.

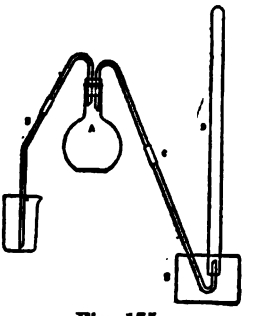

Fig. 175.

The nitrate solution is boiled until all air is expelled from the flask and tubes; C is then closed and the ferrous chloride solution in F drawn in by momentarily stopping the boiling. B is closed and C opened, and the nitric oxide allowed to pass into D, the last traces being carried over in the steam. Any carbon dioxide or hydrochloric acid accompanying the nitric acid is absorbed by the sodium hydrate.

The measuring tube is transferred to a trough of water, the volume of nitric oxide read, and the weight of nitric acid calculated.

Various modifications of the above fairly accurate but rather difficult process have been published.

Schloessing.* The concentrated solution of the nitrate is mixed with a cold solution of ferrous chloride and hydrochloric acid in a flask through which is conducted a current of pure carbon dioxide. The nitric oxide evolved on boiling, with perhaps some hydrochloric acid, is passed into a gas-tube containing potassium hydrate solution, the hydrochloric and carbonic acids being retained by the alkali. The residual nitric oxide is then mixed with a slight excess of oxygen, forming nitric acid; this is absorbed in water and titrated by standard alkali.

Morse and Linn measure the reducing power of nitric oxide. The nitrate is decomposed by acid ferrous chloride in a flask in a current of carbon dioxide. The nitric oxide is caught in a strong solution of standard potassium permanganate which reoxidizes the gas to nitric acid and retains it — $3K_2Mn_2O_8 + 5N_2O_2 = 5N_2O_5 + 3K_2O + 6MnO$. A known volume of the permanganate solution receives the gas, and after the operation is concluded there is added of standard oxalic acid solution a volume which would reduce all of the original permanganate, and the excess of oxalic acid titrated by standard permanganate.

B. In the process of Gooch and Gruener the nitrate is decomposed by hydrochloric acid in presence of manganous chloride; the chlorine evolved is passed into a solution of potassium iodide liberating an equivalent of iodine which is then titrated by standard sodium thiosulfate and starch.

C. Gattner's method. If a nitrate be heated with phosphorus acid, sulfuric acid and ammonium chloride, the nitric acid is reduced to nitrogen —

$$2KNO_3 + P_2O_3 + 2NH_4Cl = 2N_2 + P_2O_5 + 2KCl + 4H_2O.$$

The decomposition is effected in a flask connected to a washing flask containing sodium hydrate solution, this to a cylinder fitted up like a wash-bottle and completely filled with water. The exit-tube of the cylinder enters an empty measuring jar. The sample of nitrate with the phosphorus acid and ammonium chloride is placed in the evolution flask, dilute sulfuric acid run in, and the mixture warmed. The nitrogen, with some hydrochloric acid vapor,

* Chem. News, 1893—2—40.

passes through the alkali which absorbs the acid, into the cylinder forcing out an equal volume of water into the measuring jar. Finally the volume of water in the jar is read; this may be assumed to equal the volume of the nitrogen, but to correct for solubility, etc., a previous experiment on pure potassium nitrate is made the basis of the calculation. The temperature of the water at the close of the operation must be brought to that at the beginning.

D. Ulsch. The sample is allowed to stand for a time in contact with reduced iron (iron in fine powder) and dilute sulfuric acid. The nascent hydrogen converts the nitric acid to ammonia — $N_2O_5 + 16H = 2NH_3 + 5H_2O$. Then an excess of magnesia is stirred in, and the freed ammonia distilled into dilute sulfuric acid. The process is modified by Schmidt who proposes a mixture of powdered iron and zinc and acetic acid instead of iron and sulfuric acid, and by Krueger who substitutes tin in spongy form, and a solution of stannous chloride in hydrochloric acid. The Halle Station advocates a mixture of zinc dust and iron filings and solution of sodium hydrate.

E. Monnier. The solution of the nitrate is mixed with tartaric acid and brought in contact with a certain quantity of sodium-amalgam in a special apparatus. The hydrogen evolved by the oxidation of the sodium in the amalgam is passed into a gas-measuring tube and measured. A determination of the hydrogen evolved by the same amount of sodium amalgam with tartaric acid is made; the difference between the two readings is the volume of hydrogen that is combined with the nitrogen of the nitrate to form ammonia, this uniting with tartaric acid to form ammonium tartrate —

$$7Na_2 + 2NaNO_3 + 9H_2C_4H_4O_6 = 8Na_2C_4H_4O_6 + (NH_3)_2C_4H_4O_6 + 6H_2O.$$

For the separation of nitric and ammoniacal nitrogen from organic nitrogen, the nitric acid is determined by one of the common methods; then another portion of the material is percolated by a weak solution of tannin which combines to insoluble compounds with all the soluble organic nitrogenous matter, while the nitrates and ammonia compounds are dissolved. The nitrogen is determined in the filtrate and residue.

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*Hygroscopic water** is determined as usual by drying at 100° to 110°. In the absence of combined water, the loss on igniting the sample to redness in the air is organic matter and carbon dioxide, and on deducting the latter, found by another experiment, the difference may be put down as *organic matter*.

Carbon dioxide. Most mineral phosphates carry calcium carbonate in varying quantities. The carbon dioxide is best determined by boiling the sample with dilute sulfuric acid, passing the gas into potash bulbs (preceded by a drying tube), and noting the increase in weight.

Silica. The usual method for the determination of this compound must be modified where fluorine is a constituent, since, on dissolving the sample in hydrochloric acid and evaporating, part of the silica will combine with the fluorine and volatilize as hydrofluosilicic acid. The phosphate is fused with sodium carbonate and the melt extracted with water; sodium silicate, fluoride, aluminate and carbonate enter the solution. After filtering from calcium carbonate, the filtrate is heated with ammonium carbonate, when most of the silica and aluminic hydrate precipitate. The remainder of the silica may be

* Chem. News, 1891—1—100, 114, and 122.

thrown down by a solution of zinc oxide in ammonia. The separation of the silica from the alumina and zinc oxide presents no difficulties.

Fluorine. Here the problem is the separation of fluorine from silica, alumina, and calcium phosphate. The sample is fused with sodium carbonate and silica and the fusion extracted with water. The silica is precipitated by ammonium carbonate and the liquid filtered. In the filtrate the fluorine, phosphoric acid, and carbonic acid are precipitated as calcium compounds by addition of calcium chloride.

After filtration the precipitate is dried and evaporated with dilute acetic acid which converts the calcium carbonate into soluble calcium acetate; the calcium fluoride and phosphate are not affected. After lixiviation there remains a mixture of calcium fluoride and calcium phosphate, which is ignited and weighed. The precipitate is then dissolved in acid and the phosphoric acid determined gravimetrically. From the phosphoric acid is calculated the corresponding calcium phosphate, and this subtracted from the total weight leaves that of the calcium fluoride. From the calcium fluoride is calculated the weight of the fluorine.*

Calcium, owing to the association of phosphoric acid, cannot be precipitated as oxalate from the acid solution by ammonium oxalate and ammonia. But if the solution be allowed to remain faintly acid the precipitate will be nearly pure calcium oxalate, while the loss by incomplete insolubility will not be serious.

The precipitation of calcium by sulfuric acid and alcohol gives good results, and the filtrate may be used for the determination of iron and aluminum.

Iron and *aluminum.* In a direct precipitation by ammonia or ammonium acetate, the precipitate of iron and aluminum phosphates contains calcium phosphate, which, however, can be held up in great measure by a sufficient quantity of ammonium chloride. It is well after filtering, to dissolve the precipitate in acid and repeat the precipitation; or to previously remove the calcium by sulfuric acid and alcohol.

On washing the phosphates of iron and aluminum there is lost some of the combined phosphoric acid, and hence if the precipitate is weighed as the normal phosphates the calculated results for the metals will be too low. The only safe procedure is to dissolve the weighed precipitate and determine the phosphoric acid and call the difference iron and aluminum oxides.†

Krug and McElroy obtain a nitric acid solution of the metals and remove the phosphoric acid by precipitation as ammonium phosphomolybdate. The filtrate is treated by ammonia in the cold, the ammonic molybdate remaining in solution while ferric and aluminic hydrates precipitate. A repetition of the process is advised in presence of much calcium.

Sodium. In the determination of potassium the filtrate from the potassium platinchloride contains the sodium as chloride with the excess of chloroplatinic acid. The filtrate and washings are evaporated in a wide-mouth Erlenmeyer to dryness. By adapting a cork carrying two bent tubes a current of moist hydrogen is passed over the residue which is kept at 100°. When the residue has become black from the reduction of the sodium platinchloride and chloroplatinic acid to metallic platinum, a little water is added, evaporated to dryness, and hydrogen again transmitted. The moistening and evaporation are repeated until the reduction is complete, proved by the aqueous solution no

* Wiley, Agricultural Anal. 2—130.
† Chem. News, 1897—1—150.

longer showing a yellow tint. The sodium chloride is lixiviated from the residue by water, evaporated to dryness, and weighed.

Sulfocyanic acid is found in some samples of superphosphate. This compound is desulfurized by potassium permanganate as in the equation —

$$5HCNS + 3K_2Mn_2O_8 + 7H_2SO_4 = 5HCN + 6KHSO_4 + 6MnSO_4 + 4H_2O.$$

but secondary reactions may intervene in the titration by standard permanganate, hence a parallel titration is always made on a potassium sulfocyanide solution of ascertained strength and the results of the assay calculated on that basis.

THE ALCOHOLS.

Alcohol is the generic term for a number of organic bodies derived from hydrocarbons by the substitution of hydroxyl for hydrogen, and when acted on by an acid split up to form an ether and water; thus —

$$2CH_3OH \text{ (methyl alcohol)} = CH_3.O.CH_3 \text{ (methyl ether)} + HOH.$$

Methyl alcohol is a colorless volatile liquid of a specific gravity of .802 and boiling point about 56° Cent. It forms a definite compound with calcium chloride and reacts with oxalic acid to form methyl oxalate, these properties availed for the purification of the commercial article. Wood spirit is a complex liquid containing methyl alcohol, acetone, aldehyd, methyl acetate, dimethyl and allyl alcohols, etc. The best commercial grade contains about 95 per cent of methyl alcohol, commoner articles from 75 to 90 per cent, and the crude from 40 to 60.

Ethyl alcohol or shortly alcohol, may be considered as the hydrate of ethyl, $C_2H_5.OH$; it is a colorless mobile liquid boiling at 78.4°, and of a specific gravity of .7895 at 15.5/15.5° Cent. Crude alcohol ('feints') is a mixture of alcohol and water, and contains also from traces up to one per cent or more of aldehyd, acetic acid, oily and resinous bodies, etc.

Amyl alcohol $C_5H_{11}.OH$, is a colorless liquid boiling at 132°, and of a specific gravity of .8184. It is the main constituent of the complex liquid known as fusel (fousel) oil, a deleterious concomitant of newly made liquors.*

The methods of determination given below apply to the commercial ethyl alcohols and also to the distillates from alcoholic beverages, practically mixtures of alcohol and water.

Physical methods.

1. By density. The percentage of alcohol can be found with reasonable accuracy from the specific gravity in a pure mixture of alcohol and water, and also, though with a proportionately greater error, in mixtures containing moderate amounts of other constituents. Since there is a considerable contraction in volume when alcohol and water are mixed (100 volumes of absolute alcohol plus 60 volumes of water making only 154 volumes), the proportion of alcohol does not vary inversely with the gravity; so that the percentage of alcohol corresponding to any given gravity must be found from tables based on direct experiments.

Any of the usual methods of observing the specific gravity may be employed; the simplest is by the alcoholometer, a hydrometer graduated to show percentages of absolute alcohol V/V at 60/60° Fahr. Since the other constituents of commercial alcohol are in comparatively small amounts, a gravity test is sufficiently exact for a commercial assay, but in fermented beverages the extractive matter, sugar, etc., preclude its employment without previous distillation.

The distillation is made from a glass or metal retort or distillation-flask provided with a well-cooled worm. For the stronger wines and distilled liquors the receiver is connected to the condenser air-tight and is provided

* Journ. Anal. Chem. 4—29.

with a water-seal; these precautions against evaporation of alcohol from the distillate are unnecessary in distilling the lighter wines and beers, where the receiver need only be loosely closed by a cork or the body of the condenser. But invariably the connection of the still to the condenser must be steam-tight, and the worm ample in surface to insure complete condensation.

Beer and the lighter wines are distilled without other preparation than to neutralize any free acid by potash or calcium carbonate. Stronger wines are diluted with one or two, and distilled liquors with five to ten volumes of water. The distillation need never be carried to dryness, for if the alcoholic strength of the original is low or made so by dilution, practically all the alcohol will pass over into the first half or two-thirds of the distillate. A graduated cylindrical receiver is convenient for observing approximately the ratio of the distillate to the original volume.

The quantity of liquid to be distilled and the capacity of the apparatus depends on the method of taking the gravity of the distillate; usually from 100 to 300 Cc. will suffice.

The same principle is applied in a different way in an old method now but little in use. It depends on the increase in gravity of wine or beer when the alcohol is removed and replaced by an equal volume of pure water. The gravity is observed at 15° Cent. and a measured volume boiled until all the alcohol is driven off. The liquid is then made up to exactly the original volume with distilled water reducing the temperature to 15°, and the gravity again observed.

Now had the original volume of wine been distilled to dryness, the distillate, containing all the alcohol and water of the wine, would have a specific gravity g from which the proportion of alcohol contained could be ascertained by reference to the published tables of the gravity of all concentrations of dilute alcohol. The value of g may be computed from the above data, it equaling $G + 1 - G'$, where G is the gravity in the first observation, and G', that of the second. Several sources of error vitiate the accuracy of the method.

2. Several other physical attributes can be applied for the determination of alcohol. Traube * assays spirit, up to ten per cent by weight, by the 'stalagmometer'. This is a small pipette with a capillary orifice delivering the contents in uniform drops. The number of drops of water at 15° Cent. is called a, the size of the drops diminishing and their number increasing as alcohol is contained in the water. Traube's table, compiled on the basis of $a = 100$ at 15°, shows the number of drops corresponding to each .2 per cent of alcohol by weight at temperatures of 10° to 80°. Thus, a ten per cent spirit at 15° furnishes 148 drops; at 80°, 155 drops. Wines and beers are distilled before testing; the small amounts of ethereal oils, glycerol, etc., coming over are without influence on the number of drops.

3. Rakowitch, for an approximate determination, proposes to measure the expansion of a measured volume of chloroform through absorption of alcohol on shaking up with a spirit. The increase is said to be in direct ratio to the percentage of alcohol.

4. The boiling point of a spirit varies inversely with the proportion of alcohol contained; thus, absolute alcohol boils at 174° Fahr., a five per cent spirit at 205°, water at 212°. The barometric pressure must of course be considered in a determination. Moderate amounts of extractive matter do not materially affect the boiling point.

5. The temperature of the vapor of a spirit is lower in proportion to the

* Berichte, 20—2824; Chem. News, 1888—1—39.

concentration of alcohol in the vapor. Thus, if the vapor temperature is 210° Fahr., the condensed vapor will contain 13 per cent of alcohol and the concentration of the original spirit is one per cent; while if the vapor temperature is 170°, the distillate will contain 93 per cent of alcohol and the original liquid 92 per cent (Gruening).

6. Various other methods are based on viscosity, dilatation by heat, vapor density, etc.

Chemical methods.

These depend for the most part on the conversion of alcohol into acetic acid by strong oxidizers, or further into carbon dioxide and water. One molecule of alcohol yields one molecule of acetic acid or two molecules of carbon dioxide. Owing to the high reducing power of alcohol, the weight that can be treated in a determination is comparatively very small, a serious disadvantage.

1. Roese's process.* About five grams of the spirit, diluted with water to a concentration of about one per cent of alcohol, is treated with 50 Cc. of a one-per cent solution of potassium permanganate and 20 Cc. of concentrated sulfuric acid. The alcohol is immediately oxidized to carbon dioxide and water. The excess of permanganate is determinable by reduction with standard oxalic acid, the excess of the latter titrated back by permanganate.

2. Treated with potassium bichromate and dilute sulfuric acid, alcohol is oxidized, first to aldehyd, then to acetic acid. Bourcart heats the alcohol with dilute sulfuric acid and a weighed amount of potassium bichromate in a sealed tube for two or three hours. The reaction is

$$3C_2H_6O + 2K_2Cr_2O_7 + 8H_2SO_4 = 3HC_2H_3O_2 + 2K_2SO_4 + 2Cr_2(SO_4)_3 + 11H_2O.$$

The excess of bichromate is determined by the addition of potassium iodide, when iodine is liberated—

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 = 3I_2 + 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O.$$

The iodine is titrated by sodium thiosulfate.

A modification of the above employs chromic acid in sulfuric acid as an oxidizer, heated for five minutes in a flask to 98° Cent. (at which temperature it is claimed there is no reaction between the chromic and sulfuric acids at the specified concentrations), reducing the excess of the chromic acid by ferrous sulfate, and titrating back by permanganate or bichromate.

Small quantities of ethyl alcohol can be converted by oxidizers, such as potassium permanganate, ammoniacal solution of copper oxide, etc., into acetic acid, the liquid distilled, and the acid determined by titration. An amount of spirit containing not above .1 gram of alcohol is compounded with a solution of bichromate of potassium in sulfuric acid and digested in a closed flask at 100° for two hours. To prevent further oxidation of the acetic acid, the excess of chromic acid in the liquid is reduced to chromium sulfate by metallic zinc, then the liquid is distilled to dryness, water added to the residue and again distilled. The united distillates are titrated by sodium hydrate and phenol-phthalein.

If any sulfuric acid is carried over into the receiver mechanically it will react with the alkali and be counted as acetic acid. To correct for this the distillate is tested before titration by neutral barium chloride, any sulfuric acid producing a precipitate of barium sulfate, at the same time liberating hydrochloric acid equivalent in neutralizing power. The barium sulfate is filtered off and weighed, and for each 233 parts is deducted 92 parts of alcohol.

(The calculation by which this proportion is arrived at is as follows: in round numbers the molecular weight of barium sulfate is 233; of sulfuric acid 98; of

* Zeits. angew. 1888—81; Chem. Zeit. 1891—847; Journ. Amer. Chem. Socy. 1898—293.

acetic acid 60; and of ethyl alcohol 46. Let w be the weight of sulfuric acid neutralized by one Cc. of the standard alkali, then $\frac{60w}{49}$ is the corresponding weight of acetic acid neutralized by one Cc.

One gram of barium sulfate is formed from $\frac{98}{233}$ gram of sulfuric acid, and $\frac{98}{233w}$ is the volume of alkali required to neutralize the latter. The weight of acetic acid is then $\frac{60w}{49} \times \frac{98}{233w}$ grams. Since 60 parts of acetic acid are yielded by 46 of alcohol, $\frac{60w}{49} \times \frac{98}{233w} \times \frac{46}{60} = \frac{92}{233}$ grams of alcohol corresponding to one gram of barium sulfate.)

3. Monell describes a colorimetric method. A mixture of cobaltic nitrate solution and an alcoholic solution of ammonium sulfocyanide has a deep blue color which disappears when the mixture is diluted with a sufficient proportion of water. To a measured volume of the reagent is added the sample until the tint is but faint, then a mixture of alcohol and water is tentatively made up so that a volume equal to that of the standard will produce the same tint.

An admixture of methyl alcohol with water, as in distillates or high-grade wood spirits, can be assayed by specific gravity in the same way as for ethyl alcohol. But the impurities in crude wood spirit vary too much to allow any reliable conclusions to be drawn from the specific gravity.

Strong oxidizers convert methyl alcohol first to formic acid, then to carbon dioxide and water —

$$3CH_4O + 3O = 2HCHO_2 + H_2O; \text{ and } HCHO_2 + O = CO_2 + H_2O.$$

With potassium bichromate and sulfuric acid there is entire oxidation to carbonic acid. If standard bichromate solution be employed the chromic acid in excess may be reduced by standard ferrous sulfate and the excess of the latter titrated back by bichromate. Since under these conditions ethyl alcohol is oxidized only to acetic acid, mixtures of methyl and ethyl alcohols may be treated by these reagents, the weight of bichromate that has reacted determined as above, and the acetic acid distilled and titrated by standard alkali.

In the assay of wood spirit the methyl alcohol may be determined by conversion to methyl iodide —

$$5CH_4O + 3I + PI_3 = 5CH_3I \text{ (methyl iodide)} + H_3PO_4 + H_2O.$$

Phosphorous iodide is placed in a dry flask and the wood spirit dropped in, followed by a solution of iodine in hydriodic acid. After heating for some time to 80°, the liquid is distilled, finally passing a current of air through the apparatus to carry the vapor and what remains dissolved in the liquid into the receiver. The distillate is shaken up with water in a graduated tube, and the volume of methyl iodide read. Any methyl acetate in the spirit is also decomposed to form methyl iodide, and its amount, calculated from a previous determination, is to be deducted. Acetone also is found in the distillate, but may be washed out by water, correcting for the methyl iodide dissolved in this operation.

Instead of measuring the volume of the product it can be decomposed by solution of sodium hydrate in alcohol ($CH_3I + NaOH = CH_3OH + NaI$), the

alcohol evaporated off, the aqueous solution of the residue acidified by nitric acid, and the iodine of the sodium iodide titrated by standard silver nitrate solution.

For a determination of small amounts of methyl alcohol in ethyl alcohol, the former is concentrated by three successive distillations into a comparatively small quantity of the latter. By this operation certain impurities are eliminated. In each distillation about two-thirds of the liquid is brought over. In the first the liquid is made alkaline; in the second the first distillate is made acid; and in the third the second distillate is dehydrated by potassium carbonate. In the final distillate the ethyl and methyl alcohols are, after dilution, determined by specific gravity and also by the bichromate process, distilling and titrating the acetic acid. Should no methyl alcohol have been present in the sample the results will practically agree, otherwise the latter test will show proportionally lower since methyl alcohol is oxidized to carbon dioxide, not acetic acid.

The basis of another method is that anhydrous methyl alcohol forms a compound with dry calcium chloride ($CaCl_2.4CH_4O$) which is not broken up at the temperature of 100°. The sample is first dehydrated by distillation from anhydrous potassium carbonate, and the distillate allowed to stand for some time over dry calcium chloride. On again distilling, the methyl alcohol compound remains in the flask while the ethyl alcohol passes over; on treating the residue with water it is decomposed to methyl alcohol and calcium chloride.

The specific gravities of the iodides of methyl and ethyl differ considerably, and a determination can be made by preparing the iodides by compounding the spirit with iodine and red phosphorus. The gravity of the mixed iodides is observed by the usual methods, and the proportion of the constituents calculated.*

Amyl alcohol. This compound is oxidized to valeric acid by chromic acid —

$$C_5H_{11}.OH + O_2 = HC_5H_9O_2 + H_2O.$$

From a dilute aqueous solution, that may also contain ethyl alcohol up to a certain percentage, and extractive matter, the amyl alcohol is extracted by shaking three times with purified chloroform. The chloroformic solution is washed with water to remove ethyl alcohol and other soluble matters, then digested with a solution of potassium bichromate in sulfuric acid. Valeric acid is formed and is separated from the excess of chromic and sulfuric acids by distillation; the distillate is chloroform and water and contains all the valeric acid and usually also some hydrochloric acid from a reaction between chloroform and chromic acid. Digestion with barium carbonate, removal of chloroform by evaporation, and filtration, leaves a solution of only barium valerate and chloride.

The solution is evaporated and the residue weighed; it is dissolved in water and the solution divided into two equal parts. In one is determined the barium, in the other chlorine. From the weight of barium is subtracted the weight of barium calculated to combine with the chlorine, and from the remainder is calculated the equivalent weight of valeric acid and of amyl alcohol.

Dupre proceeds to oxidize the previously distilled alcohol by chromic and sulfuric acids, reduces the excess of chromic acid by zinc, and distills. In the distillate the volatile acids are neutralized by sodium hydrate, the solution

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* Zeits Angew. 1898—125.

concentrated, and the sodium salts decomposed by sulfuric acid. The acids are again distilled and in the distillate converted to barium salts, then the combined barium determined. Since barium valerate contains 40.41 per cent of barium, and barium acetate (coming from the ethyl alcohol) 58.72 per cent, the proportion may be approximately calculated (page 171).

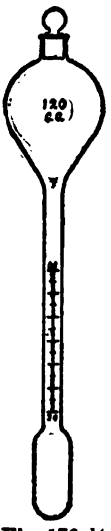

Fig. 176. 1/5

From ethyl alcohol diluted with water to a prescribed concentration, amyl alcohol is extracted by chloroform which proportionately increases in volume. Roese's apparatus, Fig. 176, has a lower bulb of a capacity of 20 Cc. to the lowest mark on the stem. Above the mark the tube is graduated in 1-20th Cc. to 26 Cc. The upper bulb has a capacity of about 200 Cc. and is marked for a total content of 120 Cc. Chloroform at 20° Cent. is poured in up to the 20 Cc. mark, then 100 Cc. of the sample to be tested (previously diluted to a concentration of 80 per cent of alcohol), and a little dilute sulfuric acid. The apparatus is stoppered and well shaken, the temperature of the liquid brought to 20°, and the increase in volume of the chloroform read on the scale.

Stutzer and Maul concentrate fusel oil into a smaller bulk of alcohol by fractional distillation before the test is made. Hertzfeld substitutes carbon tetrachloride for chloroform, and brine for water when diluting the spirit. Various other modifications have been made in the process which like all others for this determination is unsatisfactory at best.

Bardy mixes the sample with brine and extracts the isobutylic and amylic alcohols by carbon disulfide. The solution, containing also some ethyl alcohol, is in turn extracted by a little monohydrated sulfuric acid. Through the acid is blown a current of air to remove any carbon disulfide; it is then mixed with glacial acetic acid and boiled under a reflux condenser. The ethers of the higher alcohols are now floated by brine, and their volume measured in a narrow graduated tube.

If crude alcohol be diluted with water to a concentration of 30 per cent alcohol and shaken up with chloroform, in the lower layer are amylic alcohol, acetal, aldehyd, and isobutyl alcohol; in the upper are ethyl alcohol, tertiary-butyl alcohol, and acetic acid.

The number of drops of a pure ethylic spirit of given concentration delivered from a pipette with capillary orifice is increased by fusel oil contained; thus, a spirit containing .01 per cent of the oil forms 1.6 more drops than a pure spirit. The test is made more decisive by concentrating the oil into a small volume of alcohol; the spirit is diluted to 20 per cent of alcohol and saturated with salt, when the oil and part of the alcohol float and can be removed, diluted, and distilled to one third. The distillate contains all the oil and is tested against spirit dosed with known proportions of the pure oil.

The height to which a spirit rises in a capillary tube is diminished by the presence of fusel oil. The 'capillarometer' is an open glass tube of .8 millimeter bore with a scale from 0 to 50 millimeters divided in half-millimeters. The spirit is diluted with water to 20 per cent of alcohol and the rise noted. Blyth found that pure alcohol of this concentration rose to 50 Mm., that containing one per cent of fusel oil to only 43.3 Mm.

For the higher alcohols in distilled liquors the coloration produced by sulfuric acid is compared with that given by an alcoholic solution of iso-butyl alcohol. To 100 Cc. of the distillate is added a little anilin and phosphoric acid and heated for an hour under a reflux condenser; the anilin phosphate forms a

non-volatile compound with the aldehyds. The liquid is then distilled to dryness and the sulfuric acid test applied to the distillate.

For the extraction of the higher alcohols from an aqueous or alcoholic solution, common salt is dissolved in the liquid until the specific gravity reaches 1.1. It is then extracted by four portions of carbon tetrachloride. The united extracts contain the higher alcohols and some ethyl alcohol. To wash out the latter, the carbon tetrachloride is shaken first with saturated brine, then with a saturated solution of sodium sulfate. The liquid is heated under a reflux condenser with chromic and sulfuric acids to oxidize the higher alcohols into their corresponding acids, and then distilled, the organic acids and usually a little mineral acid passing over with the carbon tetrachloride. In the distillate the mineral acid is neutralized by barium hydrate and methyl orange; then the organic acids are titrated by standard barium hydrate and phenolphthalein.

The hydroxyl group combined with the radical of the higher alcohols may be determined by acetylation. Acetyl chloride dissolved in chloroform reacts with the alcohol to form a neutral ester, liberating a molecule of hydrochloric acid; thus —

(1) .... $C_5H_{11}.OH$ (amyl alcohol) + $C_2H_3O.Cl = C_5H_{11}O.C_2H_3O$ (amyl acetate) + HCl.

When a chloroformic solution of acetyl chloride is treated with water there are formed hydrochloric and acetic acids —

(2) .... $C_2H_3O.Cl + H_2O = HCl + HC_2H_3O_2$.

Hence if equal volumes of acetyl chloride be acted on, the one by an equivalent of amyl alcohol, the other by water, and the resulting liquids be titrated by standard alkali —

(1) .... $HCl + KOH = KCl + H_2O$; and (2), $HCl + HC_2H_3O_2 + 2KOH = KC_2H_3O_2 + 2H_2O$.

the latter will require double the volume of standard alkali of the former.

In practice, the alcohol is treated with an excess of a chloroformic solution of acetyl chloride, and the excess of the latter decomposed by water. An equal volume of the reagent is decomposed by water. Both are titrated by standard alkali; the former will require for neutralization a less volume of alkali than the latter in proportion to the amount of alcohol reacting with the acetyl chloride.

When a higher alcohol is heated in contact with soda-lime to a temperature of 300°, hydrogen is quantitatively evolved from the alcoholic hydroxy-groups, *e. g.* —

$C_{16}H_{33}.OH$ (cetyl alcohol) + $NaOH = NaC_{16}H_{31}O_2$ (sodium palmitate) + $2H_2$.

The alcohol and soda-lime are held in a glass tube set vertically in an air-bath and connected at the top with a U-form gas-measuring tube filled with mercury.

The rapidity with which a commercial ethyl alcohol loses the color imparted by a little potassium permanganate is roughly in proportion to the amount of impurities present. When two or three drops of centinormal permanganate are added to ten cubic centimeters of pure alcohol, reduction takes place in about ten minutes. This test is of use to those requiring a fairly pure alcohol for manufacturing purposes.

Acetone is contained in crude methylene or wood spirit to the extent of 20 per cent or more, but is largely eliminated during the refining processes. Commercial ethyl alcohol contains much less than commercial methyl alcohol, though always an appreciable quantity.

A characteristic reaction of acetone is that taking place with iodine and an alkali, yielding iodoform and an acetate —

$$CH_3.CO.CH_3 + 3I_2 + 4KOH = CHI_3 \text{ (iodoform)} + CH_3.COOK + 3KI + 3H_2O.$$

Iodoform is a yellow powder melting at 119°, slightly volatile at ordinary temperatures, and soluble in alcohol and ether.

For a gravimetric determination, one Cc. of commercial wood spirit is mixed with an excess of sodium hydrate, then with iodine and potassium iodide, both in concentrated aqueous solutions. The iodoform separates as a powder and is extracted by ether, the ether allowed to evaporate spontaneously, and the iodoform dried over sulfuric acid and weighed. No free iodine enters the ether as all the excess has been converted by the potassium hydrate into potassium iodate and iodide. Should the sample of spirit contain above 1.5 per cent of acetone, it is to be diluted with water previous to the test. A minute amount of potassium iodide will dissolve in the ether, and some tarry matter from a crude spirit, both increasing the weight of the iodoform; these are in a measure neutralized by the retention of iodoform in the aqueous solution and its volatility. The efficiency of the method in presence of aldehyd or ethyl alcohol and for crude spirit has been questioned by Vignon.*

The application of this reaction to volumetric processes has been the subject of much investigation and controversy. All the volumetric methods rest on the direct or indirect measurement of the residual iodine from a known weight compounded with the acetone.

Messinger compounds 20 to 30 Cc. of normal potassium hydrate with 1 to 15 Cc. of wood spirit in a stoppered flask. A measured excess of N/5 iodine solution is run in and the flask well shaken. The mixture is acidified by hydrochloric acid and the excess of iodine reduced by sodium thiosulfate solution with starch paste as indicator, then the residual thiosulfate titrated back by standard iodine.

According to Vignon, in the presence of water two reactions may follow the bringing together of acetone, iodine, and alkali, viz.: —

$$CH_3COCH_3 + 3I_2 + NaOH = CH_3CONaO + CHI_3 + 3NaI + 3H_2O; \text{ and}$$
$$3I_2 + 6NaOH = 5NaI + NaIO_3 + 3H_2O.$$

and to the extent of the latter reaction the amount of iodine to convert the acetone to iodoform must be increased; it is favored by the presence of methyl and ethyl alcohol and retarded by aldehyd.

Squibb,† for the assay of commercial acetone, instead of the standard solution of iodine would liberate the element *in situ* from sodium hypochlorite and potassium iodide, thus $NaOCl + 2KI + H_2O = I_2 + NaCl + 2KOH$. The method is to mix the acetone with an alkaline solution of potassium iodide, then titrate the mixture by standard sodium hypochlorite. The end-point is where a blue color is developed when a drop of the titrate is mixed with a drop of starch paste containing sodium bicarbonate. He confirms the statement that ethyl alcohol or small amounts of paraldehyd do not interfere.

Kebler ‡ modifies the above by mixing the acetone with potassium iodide, sodium hydrate, and excess of standard sodium hypochlorite. The solution is acidified by hydrochloric acid and the residual iodine determined by adding an excess of standard thiosulfate and titrating back by standard sodium hypochlorite and starch-paste —

$$2Na_2S_2O_3 + NaOCl + 2HCl = Na_2S_4O_6 + 3NaCl + H_2O.$$

* Chem. News, 1890—1—166.

† Journ. Amer. Chem. Socy. 1896—1068.

‡ *Idem*, 1897—316.

Aldehyds are found in small proportions in all samples of commercial alcohol. For some purposes, as where the alcohol is to be the solvent of certain dyestuffs, any considerable amount of aldehyd is highly objectionable.

With acid sodium sulfite aldehyds form crystalline compounds that are soluble in water and alcohol but nearly insoluble in a concentrated solution of the reagent; thus —

C_2H_5OH (acetic aldehyd) $+ NaHSO_3 = Na(C_2H_3)SO_3$ (sodium ethylidene sulfite) $+ H_2O$.

This reaction can be applied to samples comparatively rich in aldehyds, washing the precipitate by a concentrated solution of the reagent, then distilling with a dilute acid.

The determination of the small quantities normal to a purified alcohol or a beverage has not yet been accomplished satisfactorily. It is attempted colorimetrically by Guyon, applying the reappearance of color in an acid solution of fuchsin previously decolorized by sodium sulfite; the comparison is made against a standard solution of acetic or ethylic aldehyd in dilute alcohol. It is doubtful, however, whether the coloration reproduced is proportionate to the aldehyd.

Wine and spirits may contain as bases ammonia, the pyridens, the amids, and certain alkaloids. After distilling the sample with a little phosphoric acid, the distillate is mixed with a dilute solution of sodium carbonate, and free and liberated ammonia distilled and Nesslerized (page 376), the result being considered as due to ammonia and amids. On again distilling with the addition of permanganate, the ammonia found is a partial yield of the nitrogen in the pyridins and alkaloids — the process is never more than approximate.

For the determination of impurities, other than acetone, in commercial methyl alcohol, Barillot mixes 10 Cc. of the sample with 15 Cc. of a solution of sodium bisulfite. After cooling, the mixture is agitated with exactly 20 Cc. of chloroform. Acetone does not increase the volume of the chloroform, but other impurities (benzols, methylol, diallyl, etc.) enter it without condensation of volume. A special tube similar to that of Roese (Fig. 176) is used to measure the expansion of the choloroform. Ordinary methyl alcohols of good quality show from one to five per cent of impurities, strong smelling samples from ten to twenty per cent.

Fermented Beverages.

These are manufactured by converting the sugar of a saccharine liquid to alcohol and carbonic acid through the action of certain organisms. Cane sugar passes first to invert sugar, then to alcohol, but glucose directly $C_6H_{12}O_6 = 2C_2H_6O + 2CO_2$. The starches of malt and potatoes are transformed by the ferment diastase to maltose, this by yeast-ferment to glucose. Besides alcohol and carbonic acid there are formed in the fermentation small amounts of the higher alcohols, succinic acid, glycerol, acetic acid, etc.

Pure wine is the fermented juice of the grape, but certain additions, as of alcohol and sugar, are considered legitimate. The normal constituents of wine are water, alcohol from six to twelve per cent, sugar, tannin, glycerol, succinnic acid, coloring matter, and traces of many other organic and inorganic bodies. Beer, made from malt, hops and a starchy cereal, contains alcohol from three to ten per cent, carbonic acid, malt extract, bitter principles from the hop, constituents of the water of brewing, etc. Distilled liquors should be only water, alcohol from 30 to 60 per cent, and traces of volatile organic ethers, etc., but various artificial coloring and flavoring matters are not uncommon. Liqueurs and cordials contain large amounts of sugar and essential oils.

The *specific gravity* is a function of the ratio of the alcohol to the water and extractive and mineral matters contained, hence the gravities of fermented liquors are usually above unity, while distilled liquors are usually below. Although affording no specific information it is useful in corroborating conclusions drawn from the results of other determinations. It is perhaps most accurately observed by the Westphal balance, approximately by the oenometer.

Acidity. All natural wines react acid from free tartaric or succinic acids, sometimes from potassium bitartrate or acetic acid; in beer the volatile acid is acetic, the non-volatile lactic and succinic; and in cider, malic. Occasionally sulfurous and salicylic acids are found.

The determination of total acidity is made as usual by titration with weak standard alkali and a suitable indicator—litmus paper for highly colored samples.

Practically all of the acetic acid passes over on repeated distillation with water, more readily in vacuo, and may be titrated in the distillate; sulfurous acid also distills, but is largely converted to sulfuric by the action of air on the vapor. In the residue are the fixed acids that may be directly titrated after dilution.

Sulfurous acid may exist in wine either as such or as an aldehyd compound. The former is titrated by iodine and starch after acidification by sulfuric acid, either directly in the wine or after distillation under carbon dioxide gas. The total sulfurous acid is then determined in another portion of the wine by decomposing the aldehyd compound by an alkali, *e. g.*, $K(C_2H_3)SO_3 + KOH = K_2SO_3 + (C_2H_3)CH$, acidifying, and titrating as before. The difference in the volumes of titrand represents the aldehyd-sulfurous acid.

A separation of *tartaric acid* and *potassium bitartrate* depends on the insolubility of the latter in strong alcohol. One hundred Cc. of the wine is evaporated to a thin syrup, and alcohol added as long as a precipitate forms. In a few hours the bitartrate (with some extractive, etc.) is filtered, washed with strong alcohol, dissolved in water and titrated by an alkali. In the filtrate the tartaric acid is precipitated by calcium acetate as calcium tartrate, which is determined gravimetrically. Or to the wine is added sufficient potassium hydrate to neutralize about one-fifth of the free acids, then five volumes of alcohol; all the tartaric acid precipitates as potassium bitartrate together with that already existing as such. The precaution of limiting the alkali is to avoid the formation of soluble potassium tartrate.

Cider is evaporated to one-tenth its volume and the potassium bitartrate and calcium salts thrown down by an equal volume of alcohol. The filtrate is made slightly alkaline by lime-water, whereupon calcium malate separates and is purified by dilute nitric acid from which calcium bimalate crystallizes.

Salicylic acid is sometimes used as a preservative for beer. Following concentration at a low heat the acid is extracted by ether or a mixture of ether and gasoline. After washing and evaporating the solvent the acid may be determined colorimetrically by the violet color struck with ferric chloride.

The *carbonic acid* in a beer or sparkling wine is always in excess of a saturated solution. The cork of the bottle is pierced by a champagne-tap or other device allowing only a slow outflow of the gas which is led through some form of absorbent and determined gravimetrically or volumetrically. The gas remaining in solution is boiled out, with the addition of a little tannin to prevent frothing, into bulbs holding barium hydrate solution; the precipitated barium carbonate is determined directly or by difference. A vacuum pump may be employed in the operation with advantage.

The *extractive matter* of wine or beer is the non-volatile organic matter con-

tained. In wine it usually ranges from 1.5 to 8 per cent, sometimes as high as 5 per cent or more; some include the glycerol in the extractive, others not. The solution-density of the extractive matter is taken as 1.039.

The customary method of determination — by evaporation and weighing the residue and deducting the ash — is beset by the difficulty common to all saccharine fluids, the attainment of a constant weight without danger of decomposition of the residue. Where this method is adopted it is important that the dish used has a level flat bottom and is of a breadth proportionate to the volume of wine evaporated; best so large that the thickness of the layer of wine does not exceed one millimeter. After evaporating 10 to 50 Cc. of wine or 5 to 10 Cc. of beer, the residue is dried at 100° to fairly constant weight — it is said that after three hours any further loss is due to volatilization of glycerol. If it be desired to include this body in the extractive, a little standard baryta-water is added before evaporation. Sweet wines are better diluted before evaporation.

Another method is that of boiling off the alcohol and other volatile matter, making up to the original volume, and taking the specific gravity at 15.5°. Tables showing the percentage of extractive corresponding to the gravity will be found in works on wine analysis. According to Schultze and Hager, the percentage of extract for beer is 260 times the specific gravity less one, and for wine is 220 times the specific gravity less one.

Riegler observes the refractive index of the wine, then boils until the alcohol is driven off, cools, makes up to the original bulk and again observes the refraction. One gram of extractive in 100 Cc. of wine increases the refraction over that of water by .00145, while the same proportion of alcohol raises it by .00068. If R be the refraction of distilled water; R' the refraction of the wine; R'' that of the boiled and diluted wine; x, the percentage of extractive; and y the per cent of alcohol; then $R' = R + .00145\,x + .00068\,y$; and $R'' = R + .00145\,x$. Whence

$$x = \frac{R'' - R}{.00145} \text{ and } y = \frac{R' - R''}{.00068}.$$

Astringent matter. The usual methods for the determination of tannin in aqueous extracts may be applied to wine. Loewenthal's is no doubt most in use and is recommended by Vogel; others give preference to various precipitation methods. Nessler and Barth remove albuminous matters by the addition of a large proportion of alcohol to the wine, then concentrate the filtrate, and precipitate by ferric chloride and sodium acetate in a conical graduated tube. After standing 24 hours, the volume of the precipitate is read on the graduations, one cubic centimeter corresponding to .033 per cent of tannin in the wine. Girard notes the increase in weight when strips of purified sheep-gut, previously soaked in water, are left in contact with the wine for a day or two.

Nitrogenous matters. The total nitrogen of wine or beer is easiest determined by Kjeldahl's method, evaporating the sample with an excess of sulfuric acid, boiling, etc. (page 306).

In distilled liquors, Mohler determines the ammonia corresponding on the one hand to the amids and saline ammonia by distillation with sodium carbonate; then that corresponding to the pyridin bases and alkaloidal matter by continuing the distillation with permanganate. In each case the distillate is Nesslerized.

Boedlander and Traube propose the determination of the peptones of wine from their influence on the constant of capillarity. The apparatus is a pipette of peculiar construction, the lower orifice greased on the sides. For pure water the number of drops to a specified volume at a given temperature is practically

constant, while even as little as .02 per cent of peptone perceptibly increases the number. Albumin and gelatin have comparatively little effect in this way.

Sugar. In unadulterated wine the sugar is wholly glucose. Cane sugar is legitimately added to champagne during manufacture, but is usually completely inverted during the long period of aging. Cordials and liqueurs are heavily charged with sucrose.

The carbohydrates of wine are chiefly grape sugar with some tartaric acid and certain unfermentable bodies; perfectly fermented wine is nearly optically neutral, while any unfermented sugar is usually laevo-rotatory. To arrive at the quantities of these constituents a somewhat complicated process is necessary, the wine being polarized after clarification by lead subacetate and sodium carbonate, and also after inversion and fermentation by yeast.

Ethers. The bouquet and flavor of a wine depend largely on the volatile esters, the taste on the fixed. Owing to their minute quantity the determination is not very satisfactory. All react with a caustic alkali with the production of an alkali salt and alcohol, *e. g.*,

$CH_3.C_2H_3O_2$(methyl acetate) + $NaOH = CH_3OH$ (methyl alcohol) + $NaC_2H_3O_2$.

The amount of alkali neutralized in the reaction corresponds to the weight of the ester.

To the wine is added a measured volume of standard alkali, the mixture boiled under a reflux condenser, and the excess of alkali titrated back by standard acid. The result is calculated to acetic ester and so expressed. In spirits, bodies of the type of aldehyd and furfurol also react with alkali, but Mohler finds that on distillation with anilin and syrupy phosphoric acid the volatile ethers pass over, while furfurol and aldehyd remain.

A separation of the volatile from the fixed esters is done by distilling the exactly neutralized wine from a retort until nine-tenths has passed over. To both the distillate and residue is added a measured volume of decinormal potash, and after standing for a time, the residual alkali is determined by back titration with an acid, using as indicator phenol-phthalein for the distillate, and blue litmus paper for the (highly colored) residue.

Coloring matter. The coloring agents of wine may be either natural (oenolin) or artificial, the latter harmless or deleterious. The intensity of the color is arbitrarily expressed as degrees of the 'vino-colorimeter'.

The most common of the artificial dyes used to heighten the color of natural wine or simulate it in factitious articles, are fuchsin, cochineal, logwood and magenta. Schemes for the detection of these and others are based on the deportment of the wine to acids, alkalies, oxidizing and reducing agents, etc. Ragnoul states that if 5 Cc. of a strong solution of soap in water be mixed with an equal volume of water and from 10 to 20 drops of wine added, the natural coloring matter will be destroyed and the mixture becomes colorless, while the color if artificial will remain.

Other means of differentiation are by the spectroscopic bands and by absorption in silk, stearic acid, fuller's earth, etc. Nessler and Barth determine rosanilin dyes by agitating the wine with ether and ammonia; the ether layer, containing the greater part of the dye, is removed and evaporated in a capsule with a thread of white wool which absorbs it. Similar threads are dyed by ethereal solutions of different amounts of rosanilin, and the relation between the colors is a rough quantitative index of the proportion of the dye.

Furfurol. This compound is not a natural product of fermentation but is believed to come from excessive local heat during the manufacture. Like the esters it is saponified by an alkali, forming a pyromucate and furfuryl acohol—

$$2C_4H_3COOH + KOH = C_4H_3O.\ COOK + C_4H_3O.CH_2OH.$$

It may be roughly determined colorimetrically by the red color developed in a solution of aniline in glacial acetic acid, the color attaining a maximum in thirty minutes. The test is said to be exceedingly delicate. Other reagents for the purpose are rosaniline hydrochloride with sodium bisulfite in dilute sulfuric acid, and xylidin in glacial acetic acid.

Inorganic matter. The ash of normal wine consists chiefly of potassium combined as carbonate, sulfate, phosphate and chloride; sodium as chloride; calcium as phosphate and carbonate. Plastered wines (those clarified by calcium sulfate) leave an ash high in sulfates. The determination is made as usual by evaporation and ignition of the residue. Sweet wines leave so much carbon on charring that to avoid loss of alkalies on calcination the char should be lixiviated before burning. The proportion of the constituents of the ash may be determined by the ordinary methods of mineral analysis.

GLYCEROL.

Glycerol (glycerine) may be considered as a triatomic alcohol having the formula $C_3H_5(OH)_3$. It is a colorless, viscid, odorless fluid of neutral reaction and has a specific gravity of about 1.265. Fixed at ordinary temperatures, it volatilizes completely at 160°. It is quite hygroscopic and mixes in all proportions with water and alcohol, but is sparingly soluble in ether. On boiling the solution in water of a strength of 70 per cent or over there is a perceptible loss of glycerol whose vapor tension is 64 Mm. of mercury at 100° and 760 Mm. Peculiar compounds known as glycerates are formed with the alkalies, earths, and lead oxide.

Physical methods of assay. For reasonably pure aqueous solutions various physical methods can be applied.

1. For specific gravity, tables have been drawn up by Gerlach, Skalweit, Strohmer and others* that agree quite well. The determination in a dilute solution presents no special difficulties, but where the sample is fairly concentrated the viscous fluid may inclose and retain air-bubbles that rise so slowly that one may have to wait for hours till they disappear; by care in pouring into the flask this may be avoided largely or entirely.

2. The refractive index of pure glycerol at 12.5° Cent. is 1.4742; of a one per cent solution is 1.3342, water at this temperature registering 1.3330. Hence with a refractometer reading to thousandths, a determination accurate within one per cent is possible.

3. In the vaporimeter pure glycerol has a vapor tension of 66, and a one per cent solution 740, both at 100° Cent. and 760 Mm. of mercury. The average difference is nearly 7 millimeters for one per cent of glycerol.

4. According to Deiss a given mixture of anhydrous phenol and aqueous glycerol always absorbs the same quantity of water up to the point of turbidity. Ten grams of the sample is mixed with six grams of crystallized phenol and the mixture titrated at 11° Cent. with a solution of 50 grams of phenol in a liter of water. Finally on continual stirring a permanent turbidity remains. Under these circumstances anhydrous glycerol requires 28.15 Cc., and a commercial article containing 28.15 per cent of glycerol with 71.85 per cent of water would require zero Cc. Adopting the formula page 16, X is the percentage of pure glycerol; Y, the percentage of 28.15 per cent glycerol; a is 29.15; b is zero; and d the volume of the titrand used.

Chemical methods. 1. On digestion with chromic and sulfuric acids of cer-

* Journ. Socy. Chem. Ind. 1889—424.

tain concentrations, the oxygen of the former consumes the glycerol to water and carbon dioxide —

$$3C_3H_8O_3 + 7K_2Cr_2O_7 + 35H_2SO_4 = 7Cr_2(SO_4)_3 + 9CO_2 + 14KHSO_4 + 40H_2O.$$

The sample of glycerine is heated with a standard solution of potassium bichromate in sulfuric acid. When the reaction is over the excess of the oxidizer is reduced by a known weight of ferrous chloride, and the excess of the latter titrated back by standard bichromate. Or the chromic solution may be standardized by addition of an excess of potassium iodide, two atoms of iodine being liberated for each atom of available oxygen —

$$K_2Cr_2O_7 + 7H_2SO_4 + 6KI = 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2.$$

and the iodine determined by titration by sodium thiosulfate and starch-paste; the chromic acid remaining after the reaction with glycerol is determined by the same process.

Several colorimetric methods have been proposed with the green color of chromic sulfate as a basis, this formed by reduction of chromic acid by glycerol in a hot acid solution.

Since the carbon dioxide is evolved in direct ratio to the glycerol, it may be collected and weighed or measured and the glycerol calculated therefrom. Some claim this to be more accurate than the volumetric process. Of course if the sample contains other organic matter decomposable by the acid mixture the results will be correspondingly high by either process.

2. In an acid solution glycerol reacts with the oxygen of a permanganate to form carbon dioxide and water —

$$5C_3H_8O_3 + 7K_2Mn_2O_8 + 28H_2SO_4 = 14KHSO_4 + 14MnSO_4 + 15CO_2 + 41H_2O.$$

The solution of glycerol is held in a flask arranged as in Fig. 166, and after the addition of an excess of potassium permanganate solution and concentrated sulfuric acid, is boiled until all the gas has passed into the potash bulb E through the drying tube D. From the weight of the carbon dioxide is calculated that of the glycerol.

3. Glycerol is converted into oxalic acid, carbon dioxide and water when boiled with a permanganate and an alkali —

$$C_3H_8O_3 + 2K_2Mn_2O_8 = K_2C_2O_4 + 4H_2O + 4MnO + K_2CO_3.$$

The solution of glycerol is made strongly alkaline by potassium hydrate, and an excess of strong solution of potassium permanganate run into the hot solution until permanently red. The excess of permanganate is reduced by sulfurous acid or hydrogen peroxide, and the now colorless liquid filtered from the precipitated manganic oxide. After boiling off the excess of the reducer, the oxalic acid in the filtrate is determined by acidifying and titrating by permanganate, or otherwise.

4. Triacetin is formed when glycerol is heated with acetic anhydride —

$$\underset{\text{Glycerol}}{2C_3H_8O_3} + \underset{\text{Acetic anhydride}}{3(C_2H_3O)_2O} = \underset{\text{Triacetin}}{2C_3H_5(O.C_2H_3O)_3} + 3H_2O.$$

And on heating triacetin with caustic soda it is saponified with the production of sodium acetate and glycerol —

$$C_3H_5(O.C_2H_3O)_3 \text{ (triacetin)} + 3NaOH = C_3H_8O_3 \text{ (glycerol)} + 3NaC_2H_3O_2.$$

The concentrated glycerol is boiled with an excess of acetic anhydride for some hours in a flask topped by an inverted condenser. The product is diluted with warm water, converting the excess of acetic anhydride to acetic acid (page 315), and the solution of triacetin and acetic acid filtered from a residue containing most of the impurities of the original glycerin. The free acetic acid is exactly neutralized with caustic soda and phenol-phthalein; a

known volume of standard caustic soda is added, the solution boiled for a short time, and the excess of alkali titrated back by standard acid. From the above equations may be calculated the percentage of glycerol in the sample. With impure samples the results are said to be much in excess of the truth.

5. In an alkaline solution glycerol forms esters with benzoyl chloride that are fairly insoluble, containing one, two or three groups of the benzoyl radical, thus $C_3H_5.(OH)_2.C_7H_5O_2$; $C_3H_5.OH.(C_7H_5O_2)_2$ and $C_3H_5.(C_7H_5O_2)_3$. It is said that .1 gram of glycerol yields .385 gram of the mixed ethers dried at 110°. It is to be remembered that benzoyl chloride forms insoluble compounds with many other organic bodies.

6. According to Wanklyn and Johnstone* glycerol and hydriodic acid react as expressed by the equation $C_3H_8O_3 + 5HI = C_3H_7I + 2I_2 + 3H_2O$.

Separation. Volatile organic bodies may be evaporated or distilled from glycerol after fixing the latter by the addition of lime and alcohol, limiting the heat to that of boiling water.

Since pure glycerol volatilizes completely at 160°, organic bodies not volatile or decomposed at this temperature are left with inorganic matter. To prevent decomposition of the glycerol into polymers less volatile, this temperature should not be exceeded. A preferable plan is to distill in vacuo; for small quantities a simple method of purification is to place the impure glycerol in one end of a bent glass tube, exhaust the air and seal the orifice, then distill into the other end.

Glycerol is found in small quantity in most soaps, and in "glycerin toilet soaps" may reach to twenty per cent or more. For a determination, the aqueous solution of a large weight of the soap is decomposed by sulfuric acid, and the filtrate from the fatty acids neutralized and concentrated by evaporation at a low heat. Or the excess of the sulfuric acid may be precipitated by barium carbonate, the filtered solution mixed with alcohol and evaporated with an occasional addition of alcohol. From the residue the glycerol is extracted by alcohol and ether and determined in one of the usual ways.

Glycerol is an invariable constituent of wine, coming from a secondary reaction in the fermentation whereby glucose yields succinic and carbonic acids and glycerol. The normal proportion of glycerol to alcohol is said to be from 7 to 14 of the former to 100 of the latter.†

The usual course of the determination is to evaporate the wine to dryness with calcium hydrate. Strong alcohol will dissolve the glycerol from the residue, leaving the sugar and succinic acid as calcium sucrate and succinate. On evaporation of the alcohol the glycerol is left in a fairly pure state except when glucose has been added to the wine. For further purification it is dissolved in absolute alcohol, mixed with ether and the precipitate filtered off, the solution evaporated, and the residue weighed.

In the method of Oliveri and Spica the glycerol is distilled and the distillate titrated by permanganate. The wine is heated on the water bath until the alcohol is driven off, and tannin and other precipitable bodies are thrown down by basic lead acetate. The excess of lead is removed by sodium carbonate, and the filtrate evaporated to a small volume, then distilled in vacuo, or in

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* Chem. News, 1891—1—251.

† Journ. Amer. Chem. Socy. 1898—881.

steam at a high temperature. The distillate is heated to 100° and standard permanganate dropped in to permanent redness, then the excess of permanganate titrated back by standard oxalic acid. Or the glycerol may be determined colorimetrically.

The analysis of a crude glycerol for technical purposes comprises determinations of the specific gravity, ash, fatty acids, organic impurities, and sulfur compounds. To distinguish crude from refined glycerine, the aqueous solution is tested by silver nitrate and basic lead acetate, neither of which produces a precipitate in the pure article.

For the manufacture of nitro-glycerine a specially pure grade is demanded which should meet the following requirements.*

(1). Aminimum specific gravity of 1.261 at 15° Cent.

(2). Should nitrify well.

(3). After nitrification the separation of the nitroglycerine should be sharp within half an hour without the separation of flocculent matter, nor should any white flocculent matter (due to fatty acids) be formed when the nitrated glycerol is thrown into water and neutralized with carbonate of soda.

(4). Should be free from lime and chlorine, and contain only traces of arsenic, sulfuric acid, etc.

(5). Should not leave more than .25 per cent inorganic and organic residue together when evaporated in a platinum dish without ebullition (about 160°) or partial decomposition.

(6). The silver test fair.

(7). The glycerol when diluted one-half, should give no deposit or separation of fatty acids when nitric peroxide gas is passed through it.

(8). A practical nitrifying test is made, following the usual process of manufacture on the large scale. The sample of glycerol is from 25 to 50 grams and the mixed acids in proportion. The nitroglycerine is decanted from the acids, washed with water and solution of sodium carbonate, and the volume measured in a graduated tube. Especially to be observed are the yield of the product, its rapidity of separation from the acids, and the absence of flocculent matter.

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* Journ. Anal. Appl. Chem. 1893—273.

THE VEGETABLE ALKALOIDS.

These are a class of organic bodies of complex formulae, all containing carbon, hydrogen and nitrogen and the majority also oxygen. A number have been produced artificially from the pyridin bases ($C_nH_{2n-5}N$) as a starting point, and from the general relationship between the two classes, it has been proposed to define alkaloids as vegetable organic bodies that are derivatives of pyridin.*

All the alkaloids are bases of a relatively weak character and unite additively with acids to form salts. Most are solid and fixed, a few liquid and volatile. Characteristic features are a bitter taste and a marked disturbing influence on the animal economy; the greater number are active poisons in small doses. Although classed together, marked differences are observed in both the chemical and physical properties of the members; some are quite stable and may be subjected to various analytical operations without decomposition, while others are rapidly broken down, even hot water alone decomposing some varieties.

Many of the alkaloids undergo hydrolysis on boiling with a dilute solution of a fixed alkali with the production of an organic acid, usually one of the aromatic series, and a base; thus—

$C_{17}H_{19}NO_3$ (piperine) $+$ KOH $=$ $C_5H_{11}N$ (piperidine) $+$ $K_2C_{12}H_9O_4$ (potassium piperate).

$C_{17}H_{21}NO_4$ (cocaine) $+$ KOH $+$ H_2O $=$ $C_9H_{15}NO_3$ (ecgonine) $+$ CH_4O (methyl alcohol) $+$ $KC_7H_5O_2$ (potassium benzoate).

Alkaloids do not exist in plants in the free state, but are usually combined with organic acids as tannates, malates, meconates, etc. Some plants contain but one variety, while in others, notably cinchona, the poppy, and aconite root, several are contained in widely different amounts. Usually the alkaloids associated in one plant have several properties in common, yet for various reasons but one or two may have an extended therapeutic use, the others being comparatively inactive or otherwise unsuitable; for example, of the twenty-one known alkaloids of opium, but one or two have an extended use in medicine.

A list of the best known varieties follows.

Name.	Source.	Radical formula.	Form.	Properties.
Quinine	Cinchona bark	$C_{20}H_{24}N_2O_2$	Amorphous	Febrifuge
Cinchonidine	"	$C_{19}H_{22}N_2O$	Crystalline	"
Cinchonine	"	$C_{19}H_{22}N_2O$	"	"
Morphine	Opium	$C_{17}H_{19}NO_3$	"	Narcotic
Codeine	"	$C_{18}H_{21}NO_3$	"	"
Narcotine	"	$C_{22}H_{23}NO_7$	"	"
Curarine	Woorara	$C_{18}H_{35}N$	"	Paralytic poison
Strychnine	Nux vomica	$C_{21}H_{22}N_2O_2$	"	Tetanic poison
Brucine	"	$C_{23}H_{26}N_2O_4$	"	Convulsive poison
Cocaine	Coca	$C_{17}H_{21}NO_4$	"	Local anesthetic
Nicotine	Tobacco	$C_{10}H_{14}N_2$	Oily liquid	Violent poison
Caffeine	Coffee, tea	$C_8H_{10}N_4O_2$	Crystalline	Stimulant

* Allen, Coml. Org. Anal. 3—2—162 *et seq.*

Name.	Source.	Radical formula.	Form.	Properties.
Theobromine	Coca	$C_7H_8N_4O_2$	Crystalline	Stimulant
Aconitine	Aconite	$C_{33}H_{45}NO_{12}$	"	Violent poison
Berberine	Barberry	$C_{20}H_{17}NO_4$	"	Tonic
Hydrastine	"	$C_{21}H_{21}NO_6$	"	"
Piperine	Pepper	$C_{17}H_{19}NO_3$	"	
Conine	Hemlock	$C_8H_{17}N$	Oily liquid	Paralytic poison
Pilocarpine	Jaborandi	$C_{11}H_{16}N_2O_2$	Crystalline	Depressive
Physostigmine	Calabar-bean	$C_{15}H_{21}N_3O_2$	"	Mydriatic
Veratrine	Wild Hellebore	$C_{37}H_{53}NO_{11}$	Amorphous	Poison
Atropine	Night-shade	$C_{17}H_{23}NO_3$	Crystalline	Mydriatic
Emetine	Ipecac	$C_{15}H_{22}NO_2$	Amorphous	Emetic
Colchicine	Meadow saffron	$C_{22}H_{25}NO_6$	"	Poison

The exact formulae of some of the above are yet unknown.

Most alkaloidal salts are soluble in water and alcohol, but insoluble in ether, chloroform, and light petroleum. They are decomposed by alkalies and the earths, the freed alkaloid separating from the liquid as a voluminous flocculent precipitate, in some cases soluble in excess of the precipitant.

Qualitative tests. Evidence as to the presence of an alkaloidal base in a solution may be furnished by a precipitate forming on addition of an alkali, the separation of a crystalline salt on acidification with a mineral acid, etc.

Color reactions. Decomposition products are formed through the action of certain oxidizing, reducing, and dehydrating reagents. Many of the products show brilliant and characteristic, though often fugitive, colors with a small fragment of the alkaloid or a drop of its solution, but it is important that the alkaloid be free from other organic matter. Among the numerous reagents that have been described are concentrated sulfuric acid, nitric acid, bromine water, solution of iodine, and concentrated sulfuric acid containing traces of nitric acid, potassium chlorate, potassium bichromate, molybdic acid, cane-sugar, etc.

For example, a solution of ammonium vanadate in sulfuric acid produces *brown* colors with aconitine, morphine, narceine, codeine, solanine, and piperine; *blue* with apomorphine and antipyrine; *green* with colchicine, quinidine, and conine; *violet* with strychnine and papaverine; *yellow* with cinchonine, quinine, and physostigmine; *red* with kairine, veratrine, brucine and atropine; and no color with nicotine and caffeine. A brown color is also given with digitalein, a green with salicylic acid, and a purple with antifebrin.

Odor. On oxidizing an alkaloid with fuming nitric acid, evaporating to dryness, and treating the residue with an alcoholic solution of potassium hydrate, peculiar odors are exhaled by a few varieties, as cocaine, eserine, delphenium.

Many of the alkaloids and their salts in aqueous solution are strongly dextro- or laevo-rotatory toward polarized light, but for several reasons the quantitative determination is seldom attempted by this process.

The physiological effect is sometimes useful as a confirmatory test. A peculiar benumbing or tingling of the lips and tongue follows contact with aconitine or cocaine, and after administration of one of the mydriatic alkaloids — atropine, conine, cocaine, etc. — the pupil of the eye is dilated, while physostigmine and members of the nux vomica species contract it. The intensely toxic power of many varieties may be exhibited by the administration of a solution or a subcutaneous injection to one of the smaller animals. The effect varies with the nature of the alkaloid, and the experimenter may observe changes in the ease and rate of respiration, a paralytic action on the nervous system, contraction of the muscles, rise or fall in temperature, or circulatory disturbance from

dilatation of the arteries, or stimulus or depression of the heart in systole or diastole. Blow-flies have been successfully used for such experiments, and the addition of a drop of a solution of certain alkaloids to stagnant water immediately paralyzes and shortly destroys the infusoria. It is said that on the addition of a drop of solution of muscarine to weak brine holding the recently excised heart of a frog, the pulsations ceased, but were re-established, after a lapse of four hours, by the addition of a drop of solution of atropine—a striking illustration of the physiological antagonism of the two alkaloids.

Quantitative analysis. A crude drug as received by the manufacturing pharmacist may be far below or above the average in alkaloidal strength, from differences in soil and climate at the place of growth, age, manner of collection and preservation, hygroscopic condition, etc. For the preparation of a tincture or a fluid or solid extract of definite alkaloidal content, either the drug itself must be assayed to decide the proper volume of menstruum to yield a preparation conforming to the official article, or the extract, that it may be concentrated if below or diluted if above the standard. Usually both are assayed, the latter as a precaution against possible mistakes during manufacture.

A generally applicable method of analysis follows, to be modified to suit particular cases.

1. The first step is the extraction of the alkaloid, in as pure a condition as practicable, from the other constituents of the plant. The following table* shows the solvent action of water, alcohol and ether on the general constituents of vegetable matter and indicates the nature of the bodies likely to accompany the alkaloid when one of these is used for extraction.

	Water.	Alcohol.	Ether.
Alkaloidal salts	Soluble.	Soluble.	Insoluble.
Other salts of inorganic acids	Mostly soluble.	Mostly insoluble.	Insoluble.
Other salts and organic acids	Soluble.	Soluble.	Mostly insoluble.
Free organic acids	Soluble.	Soluble.	Mostly insoluble.
Tannins and coloring matters	Soluble.	Soluble.	Variable.
Sugars	Soluble.	Soluble.	Insoluble.
Gums and pectous bodies	Soluble.	Mostly insoluble.	Insoluble.
Albuminoids, etc	Soluble.	Insoluble.	Insoluble.
Starch	Soluble in hot water.	Insoluble.	Insoluble.
Cellulose	Insoluble.	Insoluble.	Insoluble.
Resins	Insoluble.	Soluble.	Variable.
Fixed oils	Insoluble.	Sparingly soluble.	Soluble.
Essential oils	Insoluble.	Soluble.	Soluble.
Chlorophyll	Insoluble.	Soluble.	Soluble.

As the alkaloid is usually in combination with an organic acid, it is liberated by the intervention of a stronger base which may be an alkali or an earth, the latter preferable on account of its sparing solubility.

After mixing the powdered drug with lime or other base, the mass is treated with alcohol, hot or cold, strong or diluted, according to the nature of the

* Allen, Coml. Org. Anal. 3—2—151.

alkaloid and the vegetable matter. The solution of the alkaloid and other bodies is filtered (unless the extraction has been done by percolation) and evaporated to dryness, leaving a more or less impure alkaloidal residue.

Dialysis has been recommended to separate the crystalline active principles of opium, aconite root and belladonna, but the process has no great advantages over others more expeditious.

Volatile alkaloids may be extracted by mixing the drug with water and excess of lime or baryta and distilling into dilute hydrochloric acid. The distillate is concentrated and the alkaloidal chloride decomposed by an alkali and extracted by ether.

2. The next step is the separation of the alkaloid contained in the residue from the various other extractives. The residue is weighed, dissolved in a dilute acid, the solution filtered, made alkaline, and the filtrate agitated with several portions of ether or chloroform which abstract the alkaloid, leaving the impurities in the dilute acid. But where certain impurities are in the residue that are fairly soluble in both dilute acid and the organic solvent, a more extended process must be carried out. It is based on the principle that, as a rule, free alkaloids are insoluble in water but soluble in ether, chloroform and petroleum ether, while their salts are soluble in water but insoluble in the organic liquids. Hence some coloring matters, oils, fats, resins, chlorophyll, etc., are extracted from an acid solution of an alkaloidal salt by shaking with ether, and after super-saturating the decanted aqueous solution with an alkali, the alkaloid is extracted by ether, leaving other impurities — extractive matter, crystalline salts, gums — behind. If yet impure, the alkaloid may be alternately passed from ether to an aqueous acid and back to ether, though a not inconsiderable loss is suffered in each transition.

Another plan is to precipitate the neutral solution by basic lead acetate, filter, add a slight excess of ammonia, again filter, warm until the excess of ammonia is dissipated, and finally precipitate the excess of lead by hydrogen sulfide. Coloring matter, tannin, and organic acids are carried down in the neutral or alkaline solution, mechanically or in combination with lead. A small loss of alkaloids is inevitable.

In a method due to Lloyd,* the concentrated impure alkaloidal solution is ground in a mortar with a paste of a mixture of ferric hydrate and sodium bicarbonate, then triturated with chloroform. The clear liquid is decanted and the residue washed several times with small volumes of chloroform, and the united liquid and washings evaporated to dryness at a gentle heat. The residue is extracted by two per cent sulfuric acid and the filtered solution made slightly alkaline by ammonia, then extracted by chloroform. Aluminum or chromium hydrate may be substituted for ferric hydrate.

Filtration through a limited amount of bone-black will withdraw coloring matters, tannic and malic acids, and some other bodies, but generally some of the alkaloid is retained as well. In dealing with a solution containing only a minute weight of an alkaloid, a large proportion of bone-black will take up all the alkaloid, to be afterward recovered by boiling with alcohol.

The volatile alkaloids may be extracted or purified by distillation in a current of steam, receiving the distillate in dilute hydrochloric or sulfuric acid.

3. Having carried the purification as far as can safely be done, the weight of the alkaloid may be determined by evaporation, precipitation or volumetrically. The simplest method is to evaporate the solution to dryness, heat to

* Journ. of Pharm. 3—21—1144; Journ. Amer. Chem. Socy. 1892—162.

the boiling point of water and weigh, but many alkaloids are too volatile or easily decomposed by heat to allow of this procedure. If an appreciable weight of impurity is suspected, the residue is dissolved and determined as follows. It is treated with neutral alcohol, filtered, and at once titrated by a standard acid with a suitable indicator. The impurities of the residue are seldom of either an acid or basic character. The standard acid is not stronger than tenth-normal (some use as dilute as hundredth-normal) since the weight of the total residue from the amount of drug usually taken for analysis is not likely to exceed 100 milligrams.

An objection to direct titration is that the color of the indicator may be modified or overpowered by coloring matter dissolved by alcohol from the residue, and here a reverse titration by standard alkali is resorted to with advantage. In some cases the plan may be followed of adding a drop of methyl orange solution and some ether to the aqueous or diluted alcoholic solution, and proceeding with the titration by standard acid, constantly stirring the titrate during the operation. The coloring matter largely enters the ether leaving the subnatant aqueous solution comparatively light colored.

Since alkaloids differ so widely in strength, no one indicator is suitable for the alkalimetric titration of all.* A number of special indicators have been recommended, among them extracts of logwood and Brazilwood, haematoxylin, Porrier's blue, gallein, iodeosin, phloxin, etc., each well adapted to particular alkaloids. Litmus and phenol-phthalein are available for the stronger bases like quinine, nicotine and morphine, but the weaker bases, as the minor derivatives of the poppy, are neutral to them, so that the acid in their neutral salts may be titrated as if it were uncombined. Most of the mineral acid salts of the alkaloids are neutral to methyl orange, and any free acid in a solution of one of these may be neutralized by its aid. Allen states that the quinine sulfate of commerce $(C_{20}H_{24}N_2O_2)_2.H_2SO_4.aq.$ is neutral to Brazilwood, logwood and cochineal, distinctly alkaline to litmus, and strongly alkaline to methyl orange; and in titrating quinine by standard sulfuric acid the point of neutrality is reached with the former indicators at $(C_{20}H_{24}N_2O_2)_2.H_2SO_4$, and with methyl orange at $C_{20}H_{24}N_2O_2H_2SO_4$.

A committee appointed by the American Pharmaceutical Association† to investigate the question of indicators in the titration of alkaloids, studied the application of Brazilwood, cochineal, haematoxylin, lacmoid, tropaeolin 00, and indeosin; they experienced considerable difficulty in securing some of the indicators, especially tropaeolin 00 and indeosin, of a satisfactory quality; of the former none, with perhaps the exception of one sample, was sufficiently sensitive. The conclusions of the committee were

"1. Haematoxylin is the indicator par excellence for titrating alkaloids. Brazilwood and cochineal compare favorably with haematoxylin but are not as reliable in some cases; nor do they appear to be quite as sensitive.

2. Pure alkaloidal material can be titrated with satisfactory results, excepting the cinchona alkaloids. Such anomalous results were obtained with the cinchona alkaloids that we are inclined to think that the nature of these alkaloids is not fully understood.

3. The estimation of alkaloids by means of volumetric solutions can only be carried out in laboratories where daily determinations are made. If the operator is not constantly in touch with his end-reaction tints he will be unable to secure satisfactory results.

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* Druggists Circular, 1900—214; Allen, Coml. Org. Anal. 3—3—80.

† Proceedings, 1896.

4. The gravimetric results based on process *b* are quite satisfactory, and it it is with this process that the average worker will obtain the most concordant results. While the volumetric process yields good results in the hands of extremely careful workers and under the most favorable conditions, yet we feel convinced from our work that the method has not been sufficiently evolved to recommend it for general use."

The process *b* referred to in (4) is in essence the extraction of the dried drug by a mixture of ether and chloroform made ammoniacal. A portion of the decanted liquid is extracted by acidulated water which converts the alkaloid to a salt; the acid solution is made alkaline by ammonia, and the alkaloid extracted by a mixture of chloroform and ether. The solution is evaporated to dryness at a low heat and the residue weighed; then dissolved in hot alcohol, diluted with water and titrated by standard acid, preferably a reverse titration by standard alkali.

Simpler methods answer for alkaloidal tinctures and solid and fluid extracts. In that of Farr and Wright, a volume of 25 to 50 Cc. of a tincture is evaporated on the water-bath, with addition of water, until the alcohol is dissipated. What remains is acidified and filtered into a separatory funnel, washing with acidulated water. The liquid is made alkaline by ammonia, and the alkaloid extracted by chloroform. To remove ammonia, the chloroformic solution is washed with water until the washings are neutral; then the alkaloid titrated by N/20 hydrochloric acid and indeosin.

A number of reagents precipitate compounds of more or less definite composition and degree of insolubility. The precipitant may be

1. An *alkali* or *alkali carbonate*, liberating the base of the alkaloidal salt by combination with the acid, thus

$(C_{22}H_{23}NO_7)_2.H_2SO_4$ (narcotine sulfate) $+ 2KOH = 2C_{22}H_{23}NO_7$ (narcotine) $+ K_2SO_4 + 2H_2O$.

A few alkaloids are sufficiently insoluble and stable for a gravimetric determination and may be filtered, dried and weighed.

2. *Picric acid.* Many of the picrates are insoluble, or nearly so, in water and an excess of the acid, forming light yellow, crystalline precipitates. The combination is very suitable for the cinchona group, nicotine, brucine and strychnine; they should be in the form of sulfates in a concentrated but only slightly acid solution, and thrown down by an equivalent of a saturated solution of (sparingly soluble) picric acid. Instead of weighing the precipitate it is advised that it be decomposed by an alkali and the alkaloid extracted by alcohol.

3. *Tannic acid* precipitates most alkaloids, but the tannates are, as a rule, somewhat soluble in even very dilute or weak acids and ammonia. Like the corresponding picrates, the moist tannates may be decomposed by a strong base, here lead oxide or carbonate forming insoluble lead tannate; the dried precipitate is extracted by hot alcohol.

4. *Phospho-molybdic acid* in nitric acid. The phospho-molybdates are yellow and amorphous, and generally quite insoluble. Ammonium salts and many organic compounds are also precipitated by the reagent and must be absent from the solution. The compounds are not of a sufficiently constant composition for direct weighing, but may be decomposed by treatment with dilute ammonia with the formation of ammonium phosphomolybdate (soluble in ammonia) and separation of the free alkaloid which can be extracted from the residue by alcohol. Phospho-tungstic and phospho-antimonic acids give analogous precipitates, the strychnine and quinine compounds with the former reagent being particularly insoluble.

5. *Iodine.* A saturated solution of iodine in potassium iodide precipitates

most alkaloids from a dilute sulfuric solution as addition compounds of complex formulae, *e. g.*, with caffeine is formed caffeine hydriodide tetra-iodide, $C_8H_{10}N_4O_2.HI.I_4$. The precipitates are yellow or reddish brown, flocculent, usually amorphous, though crystalline when formed in alcoholic solutions, and are only slightly soluble in water but more readily in presence of an excess of the precipitant. After filtering, the precipitate may be dissolved in sulfurous acid, which converts the iodine into hydriodic acid, and the sulfate of the alkaloid extracted or otherwise dealt with.

The compound known as herapathite after its discoverer Herapath, is an iodosulfate of quinine said to have the formula $(C_{20}H_{22}N_2O_2)_4(H_2SO_4)_3(HI)_2I_4 + xH_2O$. It is a brown crystalline precipitate thrown down when tincture of iodine is compounded with a solution of quinine sulfate; the reaction may be applied for the separation and determination of quinine or as a qualitative test. When precipitated by iodine directly the compound is liable to vary in composition, and De Vrij has proposed to substitute the iodosulfate of quinoidine (an uncrystallizable alkaloid of cinchona) claiming that a definite iodosulfate of quinine is invariably formed thereby.

Bismuth potassium iodide with solutions strongly acidified by sulfuric acid yields orange-red precipitates, the majority insoluble in cold water, and the reagent has been highly recommended for strychnine and the cinchona alkaloids. Mercuric potassium iodide forms light-yellow flocculent iodomercurates in solutions free from alcohol and acetic acid; many of these are quite insoluble in dilute acids and become crystalline on standing, but their composition is not definite. The precipitates may be filtered, suspended in water, decomposed by hydrogen sulfide, and after filtering from the precipitated sulfide, treated with an alkali carbonate and extracted by ether or chloroform.

6. *Gold chloride.* Yellow crystalline chloraurates or combinations of an alkaloidal hydrochloride with auric chloride. The precipitates are well suited for quantitative determinations though somewhat unstable and rapidly decomposed; metallic gold remains on ignition. Mercuric chloride reacts in a similar manner, as does platinic chloride.

7. *Potassium permanganate.* Alkaloidal permanganates are, as a rule, very unstable, some decomposing immediately with deposition of manganic hydrate, others more slowly, while a few, as of cocaine and narceine, are comparatively permanent.

Other reagents are bromine, gallic acid, tannin, potassium chromate and bichromate, cadmium potassium iodide, tartaric acid, potassium ferricyanide, etc., but most of these are better suited for qualitative tests than quantitative determinations.

A number of the above reagents have been applied volumetrically, but several difficulties are met with, namely that the composition of the precipitates is far from constant, varying with the conditions of the experiment and necessitating the conduction of a parallel determination with each analysis; that with equivalent amounts of alkaloid and precipitant a condition of equilibrium obtains where the addition of either will produce a precipitate; and that from the absence of suitable indicators, the end-point must be taken where the precipitate ceases to fall, and as the precipitate remains suspended for a considerable time, a small volume must be filtered off and tested after each addition of the titrand. The tedious filtration may be avoided by adopting the method of reverse titration, or after filtering and washing, the precipitate may be suspended in water and titrated directly by a suitable reagent.

A free alkaloid may be dissolved in a measured volume of standard acid and precipitated by a neutral reagent such as Wagners or Meyers,* and after filter-

* Journ. Amer. Chem. Socy. 1900—18.

ing, the remaining free acid in the filtrate titrated by standard alkali and phenol-phthalein.

An alkaloid forming a stable hydrochloride may be dissolved in hydrochloric acid, the solution evaporated to dryness to remove the excess of acid, the residue taken up by water, and the hydrochloric acid combined with the alkaloid determined by titration with silver nitrate and potassium chromate. The weight of the alkaloid is calculated from the formula of the hydrochloride.

Several of the alkaloids may be determined iodimetrically with good results. A known volume of standard mercuric potassium iodide or of iodine in potassium iodide is added to the solution of the alkaloid and the liquid made up to a definite volume. Filtration is done through asbestos, and the residual iodine in an aliquot part of the filtrate found by titration with sodium thiosulfate; or the washed precipitate may be suspended in water and titrated directly.

Prescott and Gordin make the point that where the ordinary solution of iodine in potassium iodide is added at once and in large excess to the solution of the alkaloid there is precipitated the highest periodide only, which is not the case if added a little at a time. A preliminary test shows by the color of the supernatant fluid what must be the ratio between the two solutions that only the highest periodide will form. The proper volume of iodine solution is mixed at once with the alkaloidal solution, the mixture filtered, and the excess of iodine determined in an aliquot part of the filtrate by titration with thiosulfate.

The separation of the alkaloids is a problem of far greater difficulty than the separation of the inorganic bases, for besides lacking the stability of the latter, the alkaloids and their precipitable compounds have not that degree of insolubility that allows a nearly perfect separation of the metals. In practice the alkaloids to be isolated are usually members of a group derived from one natural source, and the separation is consequently more difficult since they have many properties in common and a similar deportment toward solvents and precipitants.

By reason of the varied degrees of solubility of the precipitates in water, dilute acids and alkalies, organic solvents, and an excess of the precipitating solution, several of the precipitants named above may be of service. Thus, the tannates of picrotoxin and agaricine are readily soluble in an excess of tannic acid solution, those of colchicine and digitaline insoluble but dissolved by a dilute alkali, while those of aconitine and papaverine are insoluble in either.

The compounds of a few of the alkaloids (as narcotine, papaverine, narceine) with weak acids decompose rapidly with separation of the base, and if there be added to a solution of any of their salts an excess of sodium acetate and the mixture allowed to stand for some time, all the alkaloid will be obtained as a precipitate.

The volatile alkaloids (nicotine, conine, the coniceines, lobeline, sparteine, lupeline, piturine, and spigeline) may be distilled from those non-volatile and not decomposed at the temperature of distillation. The operation is best conducted in vacuo.

The diversity in the comparative solubilities of free alkaloids in different menstrua often permits a fair, more rarely a nearly complete separation by the process of extraction by an immiscible solvent, favored by the ease with which free alkaloids are converted into their salts and vice versa. A general scheme* for the separation of alkaloids and the organic bodies usually accompanying them is given opposite, though the correctness of some of the statements has

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* Allen, Coml. Org. Anal. 3—159.

Extraction of Alkaloids and other Principles from Aqueous Liquids by Immiscible Solvents (after Dragendorff).

The liquid is warmed to about 40° or 50° C., rendered distinctly acid with *dilute sulphuric acid*, and agitated with an equal measure of *petroleum ether*, which is then separated.

- **Petroleum Ether** extracts from the *acidulated* liquid:—
  - *Bases*—
    - Piperine.
  - *Non-Basic Principles*—
    - Absinthin (incompletely).
    - Capsicum (pungent principle).
    - Hop Bitter (incompletely).
    - Salicylic acid.

- **Aqueous Liquid** is agitated at 40° or 50° C. with an equal measure of warm *benzene*, and separated.
  - **Benzene** extracts from the *acidulated* liquid:—
    - *Bases*—
      - Berberine (traces).
      - Caffeine.
      - Colchicine.
      - Piperine (residual portion).
    - *Non-Basic Principles*—
      - Caryophyllin.
      - Cascarillin.
      - Cnicin.
      - Colocynthin.
      - Cubebin.
      - Daphnin.
      - Delphin.
      - Digitalin.
      - Elaterin.
      - Ericolin.
      - Gratiolin.
      - Populin.
      - Quassiin.
  - **Aqueous Liquid** is agitated with *chloroform*, and separated.
    - **Chloroform** extracts from the *acidulated* liquid:—
      - *Bases*—
        - Cinchonine (very doubtful)
        - Colchicine.
        - Geissospermine.
        - Narceine.
        - Papaverine.
        - Quebrachine.
        - Theobromine.
      - *Non-Basic Principles*—
        - Benzoic Acid.
        - Convallamarin.
        - Digitaleïn.
        - Helleboreïn.
        - Œsculin.
        - Physalin.
        - Picrotoxin.
        - Saponin.
        - Senegin.
        - Syringin.
    - **Aqueous Liquid** is agitated once with *petroleum ether* to extract dissolved chloroform, separated, more *petroleum ether* added, then a moderate excess of *ammonia*, agitated and separated.
      - **Petroleum Ether** extracts from *ammoniacal* solution:—
        - *Bases*—
          - Aniline.
          - Conine and methylconine.
          - Conhydrine.
          - Nicotine.
          - Papaverine.
          - Quinine.
          - Sparteine.
          - Trimethylamine.
          - Bases of capsicum, pimento, and *Sarracea purpurea*, with *traces* of brucine, emetine, sabadilline, sabatrine, strychnine, veratrine, &c.
      - **Aqueous Liquid** is agitated with *benzene*, and separated.
        - **Benzene** extracts from the *ammoniacal* solution:—
          - *Bases*—
            - Atropine.
            - Aconitine.
            - Aspidospermine.
            - Brucine.
            - Codeine.
            - Delphinine and Delphinoidine.
            - Emetine.
            - Gelsemine.
            - Hyoscyamine.
            - Narcotine.
            - Pereirine.
            - Physostigmine.
            - Pilocarpine.
            - Quinidine.
            - Sabadilline.
            - Sabatrine.
            - Strychnine.
            - Taxine.
            - Thebaine.
            - Veratrine, and a *trace* of cinchonine.
        - **Aqueous Liquid** is agitated with *chloroform*, and separated.
          - **Chloroform** extracts from the *ammoniacal* solution:—
            - *Bases*—
              - Celandine bases.
              - Cinchonine.
              - Narceine.
              - Nupharine.
              - Papaverine, and *traces* of morphine, together with the bases soluble in benzene, which may have escaped extraction by that solvent.
          - **Aqueous Liquid** is agitated with *amylic alcohol* at 60° C., and separated.
            - **Amylic Alcohol** extracts from the *ammoniacal* solution:—
              - *Bases*—
                - Narceine (partly).
                - Morphine.
                - Solanine (solution gelatinizes on cooling).
              - *Non-Basic Principles*—
                - Salicin.
            - **Aqueous Liquid** (ammoniacal) retains:—
              - *Bases*—
                - Curarine.
                - Narceine and *traces* of berberine.
              - *Non-Basic Principles*—
                - Digitalin.

been questioned. The scheme can be modified to advantage when the nature and relative proportions of the members present are known.

Special methods. As illustrations of the special methods in use for the determination of the medicinally valuable alkaloids in crude drugs, a few examples are given. The first is a favored method for the assay of aconite root.

1. About 30 grams of the powdered root is percolated with 160 Cc. of alcohol of a specific gravity of .890. The percolate is evaporated to a small bulk on the water bath, and after cooling, diluted with a little water and 15 Cc. of decinormal sulfuric acid. After filtering and washing the precipitate with dilute acid, the united filtrate and washings is shaken twice with chloroform to remove coloring matter, the alkaloidal salts remaining with the acid. Any traces of alkaloid that may have passed into the chloroform are reclaimed by shaking it with a little dilute acid which is then united with the main portion. The acid solution is now made slightly alkaline by potassium carbonate and the free alkaloids extracted by chloroform; the chloroform is washed once with water to remove any potassium salts it may have taken up, then evaporated to dryness, and the somewhat impure residual alkaloids weighed.

The separation of the associated alkaloids is not an easy matter as a rule; a method proposed by Wright and perfected by Allen for the determination of the crystallizable (medicinally active) alkaloids in the residue is more feasible. The principle is that of hydrolyzing the alkaloids by heating under pressure with an alcoholic solution of potassium hydrate, yielding the potassium salts of several organic acids — thus aconitine gives potassium benzoate, potassium acetate and aconine —

$$\underset{\text{Aconitine}}{C_{33}H_{45}NO_{12}} + 2KOH = \underset{\text{Potassium benzoate}}{KC_7H_5O_2} + \underset{\text{Potassium acetate}}{KC_2H_3O_2} + \underset{\text{Aconine}}{C_{24}H_{39}NO_{10}}.$$

The alcohol is evaporated and the residual liquid acidified by hydrochloric acid; the liberated benzoic acid is then extracted by ether. The ether is washed with water until free from mineral acid, stirred up with water, and the organic acid titrated by weak standard alkali or baryta-water and phenol-phthalein.

2. A well-known method for the determination of quinine in the various kinds of cinchona bark is due to Schmidt. He macerates for 24 hours, twenty grams of the finely powdered and air-dried bark in a mixture of ten Cc. of ten per cent ammonia, twenty Cc. of ninety per cent alcohol, and 170 Cc. of ether. Of the clear solution 100 Cc. is mixed with 27 Cc. of water and three or four Cc. of normal hydrochloric acid, and set aside for 24 hours to allow spontaneous evaporation. The liquid is further concentrated on the water-bath, maintaining a slightly acid reaction by hydrochloric acid, or if too strongly acid by the base cinchonine.

After cooling, the liquid is exposed to the air until any coloring matter has separated, and after filtering, two or three grams of potassium sodium tartrate added to precipitate the quinine and cinchonidine as tartrates; the mixture is warmed on the water-bath for fifteen minutes and allowed to stand for twenty-four hours, then filtered and washed with the minimum of cold water and drained. The filtrate and washings are measured in order that a correction may be applied for the solubility of the tartrates therein.

The precipitate is dissolved in very dilute hydrochloric acid, and foreign matters extracted by shaking out several times with ether (in which the alkaloidal hydrochlorides are insoluble); the acid solution is then made alkaline by sodium hydrate and the precipitated alkaloids extracted by ether. The

ethereal solution on evaporation leaves a residue of quinine and cinchonidine to be weighed after drying at 100° to 110°.

The mixed alkaloids are now washed with a saturated solution of cinchonidine in ether which dissolves the quinine but not the cinchonidine, nor does any cinchonidine separate from the ethereal solution. The residue of cinchonidine is washed with a little pure ether, dried and weighed, and the quinine found by difference, both corrected for the solubility of their tartrates.

Cinchonidine sulfate is a common impurity of commercial quinine sulfate, and an empirical method for its determination is based on the greater volume of solution of ammonia required to dissolve cinchonidine than quinine. In practice, a weighed amount of the sample to be tested is macerated with ten times its weight of water at 15° and the solution filtered; the filtrate is a saturated solution of quinine sulfate (one gram dissolves in about 740 Cc. of water) containing also *all* the cinchonidine sulfate present in the sample since the proportion rarely exceeds one per cent. A measured portion is titrated by standard ammonia until the precipitate of quinine and cinchonidine at first formed has just dissolved to a clear fluid. The volume of ammonia in excess of that required in a parallel determination on pure quinine sulfate is in proportion to the cinchonidine sulfate in the sample.

Another method for this determination is that known as the 'optical assay' depending on the principle that the salts of both quinine and cinchonidine are laevo-rotatory to polarized light, the former to a greater extent than the latter. The procedure recommended by Koppeschaar is to convert the mixture of the alkaloids into tartrates, filter and dry the precipitate, and dissolve .4 gram in 20 Cc. of dilute hydrochloric acid. The angle of rotation is observed in the polarimeter by monochromatic light, and the percentages of the alkaloidal tartrates calculated by the general formula for mixtures, $X = 100\,\frac{d-b}{a-b}$.

Here X is the percentage of quinine tartrate; a, the specific rotatory power of quinine tartrate (—220.07°); b, that of cinchonidine tartrate (—137.67°); and d, that of the mixture polarized. The value of d is found from the equation $d = \frac{100a}{2L}$, where a is the angular rotation, and L the length in decimeters of the observation tube of the polarimeter (since of the mixed tartrates there was dissolved .4 gram in 20 Cc. of acid making a two per cent solution, and the angle of rotation observed through a tube L decimeters long).

3. For the determination of nicotine in tobacco, advantage is taken of the volatile nature of the alkaloid for its separation from cellulose, proteids, pectic and other organic acids, gum-resins, inorganic matter, etc. The method of Kiessling, somewhat modified, is as follows: —

Of powdered tobacco leaves, one hundred grams is mixed with slaked lime and distilled in a current of steam until the vapor is no longer alkaline; nicotine distills together with some ammonia formed by the action of the lime on nitrogenous matter. The distillate is slightly acidulated by sulfuric acid, evaporated to 50 Cc. (nicotine sulfate is not volatile), made slightly alkaline, and the nicotine extracted by six portions of ether. The ethereal solution is titrated by tenth-normal sulfuric acid, and the nicotine calculated from the volume required. The results are usually somewhat too high. As a check, the titrated solution is evaporated to dryness, weighed, and the nicotine sulfate dissolved from the residue of ammonium sulfate (slightly soluble in ether) by absolute alcohol. The weight of the residue is deducted from the total weight, nicotine sulfate forming the difference. Or the sulfuric acid com-

bined with the nicotine may be titrated by standard alkali and phenolphthalein, since nicotine is neutral to this indicator.

4. In morphiometry the alkaloids of the poppy (*papaver somniferum* — the exudation of the capsules of the plant) are extracted from resins, gums, coloring matter, etc., followed by their separation, or more usually the isolation of morphine alone.

In all of the numerous methods it will be noticed how minutely the directions are laid down in order that the unavoidable losses through solubility, etc., may be kept to a minimum.

Teschemacher and Smith * direct that 18 grams of pulverized opium be completely exhausted with warm water and filtered. The extract is evaporated to the consistency of a syrup at a heat not exceeding 90°, poured into a small flask and the dish rinsed with a little water. There are added four Cc. of alcohol sp. gr. .820, and forty grams of ether, the flask corked, and the contents mixed by a gentle rotation; then 3.3 grams of ammonia sp. gr. .935 is introduced and the flask well shaken to precipitate the alkaloid in a granular form. After standing for eighteen hours to complete the precipitation, the liquid is filtered by the aid of the pump, and the precipitate washed until the washings pass uncolored, first with a saturated (.33 per cent) solution of morphine in alcohol containing five per cent of ammonia, then with a saturated (.04 per cent) solution of morphine in water. The precipitated alkaloids are dried at a low heat, finally at 100°.

In order to remove the narcotine, codeine, papaverine and narceine from the morphine, the precipitate is ground in a mortar and digested and washed several times with benzene. The residue is morphine impurified by considerable coloring and other organic matter. After drying it is weighed and titrated by standard hydrochloric acid of such a concentration that ten Cc. neutralizes one gram of pure morphine with litmus as indicator. It has been proposed to simplify the assay by omitting the extraction by benzene, since litmus is stronger than the precipitated alkaloids other than morphine.

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* Chem. News, 62—93 and 103.

THE TANNINS.

The tannins are a group of amorphous astringent organic bodies of vegetable origin having many properties in common, yet differing greatly in others. They are characterized by their power to unite with gelatin to form non-putrescible compounds, their value in the arts depending chiefly on this property. Sources of tannin of commercial importance are oak; hemlock and chestnut barks, canaigre, sumach, gambier, myrobalans, gall-nuts, etc. Many of these contain two or more varieties of tannin.

All are composed of carbon, hydrogen and oxygen. Various schemes for classifying the different varieties have been devised.* That of Trimble divides them into two groups, (1) the gallo-tannins, containing about 50 per cent of carbon and 3 to 4.5 per cent of hydrogen, and (2) the oak-tannins, containing about 60 per cent of carbon and 5 per cent of hydrogen. Proctor makes three classes, namely —

"1. Derivatives of catechol, which yield no bloom, and usually give greenish-blacks with ferric acetate, and which include hemlock, mimosa, cutch, gambier, quebracho, etc.

2. Derivatives of pyrogallol, which deposit bloom in leather, give bluish-blacks with iron, and embrace galls, sumach, divi-divi, myrobalanes, pomegranite rind, etc.

3. Tannins which contain both pyrogallol and catechol, such as oak-bark and valonia, and which, as is well known, yield bloom and give blue-blacks with iron."

Regarding the chemical constitution, it is said that all varieties contain the benzene ring, while Reinitzer considers it probable that they contain oxyhydrogen groups of a phenolic character.

The tannins are soluble in water, alcohol, alcohol-ether, glycerol and acetone, but are nearly insoluble in ether, chloroform, benzol, gasoline and carbon disulfide. With alkalies they oxidize and darken; with nitric acid are oxidized to oxalic acid, almost quantitatively at a certain strength of the acid, a distinction from gallic acid which is oxidized to isotrichlorglyceric acid. Insoluble precipitates are afforded with gelatin, benzoyl chloride, and many organic bases and metallic compounds.

Extraction. For the extraction of the tannin from barks and other sources, the solvent is almost invariably water. It is usual to weigh such an amount of the powdered tan-ware that of an infusion measuring one liter, 100 Cc. shall yield on evaporation a residue of .6 to .8 gram. The temperature of the water during the extraction has an influence on the amount of tannin taken up, boiling water often abstracting less than water at a lower temperature. The infusion is made either by heating the powdered tan-ware with water in a flask and filtering; or by percolation, when the first half of the water used is at 50°, the remainder at 100°; the two are mixed, cooled to room temperature, and made up to a liter. The percolation process is to be preferred, and several forms of apparatus have been designed especially for the purpose,

* Journ. Amer. Chem. Socy. 1898—34; Prescott, Organic Anal. 466.

acting continuously or intermittently.* An aliquot part of the clear infusion is withdrawn for the tannin assay.

The color of the tan-liquor may be expressed in terms of equal-colored standard solutions of tannin, anilin dyes, and the like, but more satisfactorily according to the units of Lovibond's tintometer (page 261).†

Determination of tannin. Of the multitude of methods that have been advocated it would appear that none directly measures tannin — practically, the substance which in a cold solution converts hide to leather. No two varieties of tannin have precisely the same deportment with reagents, and further, the reactions are not limited to tannin alone but include considerable amounts of other constituents of the extract such as gallic, ellagic, gallamic, glauco-melonic acids, etc., that while possessing many of the chemical properties of tannin are of less or no value as tanning material. A few methods are measurably free from these sources of error.

The methods that have been proposed for the determination of tannin in aqueous solution may be divided into

1. Precipitation by a metallic salt or other compound, weighing the precipitate, or igniting it and weighing the inorganic residue; or the reaction is applied volumetrically.

2. Precipitation by an organic body, weighing the precipitate, or calculating from the specific gravity of the solution before and after precipitation; or the reaction applied volumetrically.

3. Oxidation of the tannin by a reagent in solution or in the solid form, with a correction for other oxidizable matters.

4. Absorption of the tannin in a solid reagent, determining it by increase in weight of the reagent, or by the difference in weight of the residues left on evaporation of the original liquid and the filtrate, or by the difference between their specific gravities.

5. Colorimetric methods based on the colors produced by the addition of certain reagents, *e. g.*, ferric salts.

6. Methods based on the refraction of light.

7. Methods based on the rotation of polarized light.

Of the many proposed methods but two can be said to have gained the confidence of the tanning chemist, namely the Loewenthal and the hide-powder methods and their modifications. For many years the former was considered to afford the nearest approach to accuracy obtainable in the tannin assay, but more recently the hide-powder method has the favor of most chemists as more nearly agreeing with tannery practice.

1. Loewenthals method is based on the oxidation of tannin by permanganic acid, it being converted into a number of oxidation products; the nature of the reaction is somewhat obscure. The oxidation proceeds slowly and irregularly, and gallic acid and other organic bodies of the leach also reduce permanganate. On these accounts a simple titration of the extract would be futile, and the practice of the process is complicated by the necessary modifications.

Sulfindigotic acid in a dilute sulfuric acid solution is rapidly and completely oxidized by potassium permanganate, the blue color passing to a pure yellow. And where a solution of a mixture of sulfindigotic acid and tannin is titrated by permanganate, the influence of the adjunction of the former causes the oxidation of the latter to proceed much more rapidly than when alone, and for this object sulfindigotic acid is introduced into the leach, the two being simultaneously oxidized during the titration.

* Journ. Socy. Chem. Ind. 1896—885.

† Leather Manufacturer, 1895—83.

To correct for the action on permanganate of the organic non-tannins, two titrations are made; the first on the extract directly, the second on another portion of the extract from which the tannin has been removed by absorption in gelatine or hide-powder. The details of the process have been considerably modified by different chemists; in essence it is as follows.

There are required three solutions of reagents; potassium permanganate that has been standardized against oxalic acid; sulfindigotic acid in diluted sulfuric acid; and gelatine in water. A volume V of the infusion of the bark to be assayed is largely diluted with water, a measured volume of the sulfindigotic acid mixed in, strongly acidified by sulfuric acid, and titrated by permanganate until the end point is shown. The titrand is run in by drops or by single cubic centimeters, and the first appearance of a faint pink tinge at the edge of the yellow liquid is taken as the end-point. This titration will require a cubic centimeters of the permanganate.

Another volume V of the leach is treated with a measured volume of the gelatin solution to precipitate tannin, and the excess of gelatine thrown down by saturating the liquid with common salt. Dilute sulfuric acid is added and a limited weight of finely powdered barytes or kaolin to facilitate the filtration. The mixture is diluted to a definite volume with water and a part filtered through a dry paper; a measured portion of the filtrate is titrated as before and the volume of the titrand required is calculated to the original volume V of the leach, this amonting to b Cc.

Then a, the volume of permanganate oxidizing the tannin, sulfindigotic acid, and gallic acid and associates, minus b, the volume oxidizing the sulfindigotic acid and gallic acid and associates, leaves c, the volume oxidizing the tannin. A correction is also to be made for the oxidizable impurities of the gelatin solution, found by a direct titration. Uniformity in the rate of addition of the titrand, rapid and continuous stirring during the titration, and a uniform temperature of the titrate are essential for concordant results.

It has been found that 62.36 grams of the tannin of oak bark reduces the same weight of permanganate as 63 grams of oxalic acid, and the weight of tannin may be calculated from this datum, but as there is some uncertainty regarding the ratio, and as the tannins of other tan-wares have different ratios, it is best to make the results comparative and report that the sample assayed contains tannin equivalent to so many grams of oxalic acid, or that it consumes so many grams of oxygen (of permanganate) per hundred grams of bark.

2. By hide powder. The methods now most in favor are based on the absorption of tannin by powdered raw hide. It will be seen that the scheme follows in a measure the technic of tanning and therefore gives comparative results. While it cannot be denied that certain substances other than tannin are also absorbed, yet the same is also the case in the tanning process. Like all other methods this must be regarded as yielding only an approximate determination of tannin itself.

The powdered hide is prepared by several manufacturing chemists. Ununiformity in quality is said to be the greatest source of errors in analysis, and some recommend mixing the powder with an equal weight of shredded filter paper to distribute the particles of powder uniformly in the container. The physical condition of a lot of hide powder indicates its quality to some extent, but the absorbent power for tannin, and freedom from matters soluble in water but precipitated by tannin, must always be ascertained before putting it into use.

As substitutes for hide have been advocated the middle coat of the intestine of the sheep, finely shredded rabbit skin, asbestos fiber, formalized gelatin,

ungummed silk, coagulated albumen, and other absorbents, but none have displaced hide. Procter states that the sawdust from the buffalo-hide pickers (a waste product of tanneries), after purification by sulfurous acid, is equal in absorbing power to hide powder, though too fine for use in the percolation process.

For the absorption of the tannin the infusion is either (1), shaken up with the hide powder and the liquid filtered, or (2), is percolated through a column of the powder.

(1). In the "shake method" from 50 to 100 Cc. of the clear cold tannin infusion is evaporated to determine total solids. To another equal volume is added washed hide powder in several portions, shaking well after each addition. The liquid is filtered and a convenient fraction evaporated and weighed; the weight is calculated for the total volume and corrected for the moisture brought in by the moist hide powder. The process is rather a tedious one but may be hastened by the use of some mechanical device for mixing the hide with the infusion; Fiebing employs the well known "milk shake" apparatus.

Fig. 177.

(2). In the "percolation method" the infusion is percolated through a cylinder filled with hide powder. The first 50 Cc. passing through is rejected, since the hide takes up gallic acid until it has come in contact with tannin; the next 50 Cc. is evaporated to dryness and the residue weighed.

Schreiner's percolator is shown in Fig. 177. The conical bulb A is filled with hide powder and pressed on the rubber stopper B. The infusion is poured into C, and rising through A empties into a beaker below D. The object of the bulb E is to collect the first flow, which is not to be used for the determination. After E is filled, the remainder of the percolate flows directly to D, not mixing with that in E. Various modifications endeavor to obviate the weak feature of the apparatus, namely the difficulty of packing A uniformly close.

Hurty,* operating on a ten per cent solution of an extract, evaporates 100 Cc. to obtain total solids. The remainder of the solution is filtered giving a filtrate (A) of which 100 Cc. is evaporated to obtain the weight of the soluble solids. Hide powder is purified from soluble constituents precipitable by tannin by percolating 100 Cc. of (A) giving a percolate (B) which is reserved for testing; the entire removal of soluble matter of the hide is tested by running through it a little of (A) and mixing the filtrate with a further portion of (A) whereupon the mixture should remain clear. If so, 100 Cc. of (A) is percolated and evaporated to obtain the weight of non-tannins. That all the tannin has been absorbed by the hide is proved by running through 5 Cc. of (A) and mixing with some of (B); any tannin contained is precipitated.

The weight of the residue from (1) or (2) is subtracted from that obtained from an equal volume of the original infusion, the difference being the weight of tannin absorbed.

Instead of weighing the residues left on evaporation, the specific gravities of the original extract and the percolate may be determined, the difference being proportional to the tannin withdrawn. Each gram of gallotannic acid in 100 Cc. of the extract is considered to increase the density by .004, this holding good up to a total of five per cent.

3. Absorption by gelatin. As gelatin and tannin unite to form an insoluble compound, more readily in presence of alum or sodium chloride, it would

* Journ. Amer. Chem. Socy. 1898—64; Leather Manufacturer, 9—10.

appear that a simple and accurate method of assay would be that of weighing the precipitate, but not only does the composition vary according to the nature of the tannin, but many manipulative difficulties are encountered. Collin and Benoist propose a volumetric method in which a standard solution of gelatin is titrated by the tannin solution using methylene blue as an indicator.

Of the many other methods that have been put forward it is unnecessary to speak in detail since none are in common use. A number of reagents combining with tannin to form insoluble compounds have been advocated, (1) weighing either the precipitate or the inorganic base left on ignition, or (2), computing from the specific gravities of the solution before and after precipitation. Lead carbonate and acetate, antimony tartrate, copper and zinc oxides, ammonium salts of copper, nickel, and zinc, certain alkaloids, certain anilin dyes, etc., are precipitants, but the constancy of the composition of the respective precipitates formed cannot be assured even when produced under fixed conditions.

Volumetric methods are based on the precipitation of the tannin by a reagent or combination of reagents; after filtering the precipitate is dissolved or suspended in water, and the reagent combined with tannin is titrated by a volumetric solution; or the precipitant may itself be a volumetric solution, and the excess in the filtrate or an aliquot part titrated. Reagents for this purpose are solutions of gelatin, lead acetate, methylene blue alone or with gelatin, potassium antimony tartrate with safranin, Porrier's green 4JE, etc., but here the same objection applies. Modifying Loewenthal, the tannin may be precipitated by ferric acetate, zinc acetate, or the like, and the precipitate dissolved and titrated by permanganate; or the solution may be titrated before and after precipitation. Colorimetric methods are based on the green or blue hues struck with ferric solutions by the tannins, and a polarimetric method has been described.

Tanning extracts.* These contain water and the soluble matter of the bark or wood. For example, extract of hemlock bark contains from 45 to 55 per cent of water, 15 to 30 of tannin, 12 to 18 of non-tannins, 2 to 10 of 'reds',† and 1 to 1.5 of ash. Various additions are made to certain extracts for technical reasons.

1. Water is determined by evaporating two to four grams of the extract in a platinum dish, and drying at 100° to constant weight.

2. Ash, by burning the residue from (1) in a place free from draughts, since the ash is very light and easily blown away.

3. Soluble matter. From 20 to 25 grams of the extract is diluted with water to one liter; some would reduce the weight of extract to about five grams per liter, claiming that a much greater residue is left with the prescribed quantities. After heating the liquid to 90°, a part is quickly filtered through cotton. The filtrate contains all constituents soluble in hot water; it is allowed to cool and 100 Cc. drawn out by a pipette into a tared dish, taking care to shake up the liquid before drawing out, since a part of the matter soluble only in hot water separates as the liquid cools. The liquid is evaporated to dryness and the residue dried at 100° and weighed; it is the matter soluble in hot water, *a*.

The remainder of the liter is cooled, filtered clear, and 100 Cc. evaporated and the residue dried and weighed; it is the matter soluble in cold water, *b*.

The difference between *a* and *b* is the matter soluble in hot water only, the 'reds.'‡

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* The Leather Manufacturer, 1895—54.

† Analyst, 1898—33.

‡ Proctor Leather Indust. Text-book, 56.

A part of the filtrate is used to determine the tannin and non-tannins by evaporating and weighing the liquid before and after filtration through hide-powder, as before described.

Valuation of leather.* The sample is finely divided by rasping, and the powder treated as follows.

1. The *specific gravity* is determined, most conveniently by finding the volume of mercury displaced by a given weight of the powder. The result is calculated on the basis of 18 per cent (the average) content of water. The mean specific gravity of 94 samples of leather showed 1.012.

2. *Water* is determined by drying at 105° to constant weight.

3. *Ash.* The inorganic matter is determined by incinerating a portion in a platinum crucible. According to Eitner it is generally about one per cent, over three per cent indicating fraudulent weighting. The ash may be examined qualitatively or quantitatively for barium, calcium or lead sulfates, sand, clay, etc.

4. *Oil* and *Grease.* These may be either natural or incorporated. From five to ten grams of the powder is extracted in a Soxhlet apparatus by petroleum ether. The extract is evaporated and the residue weighed; it may contain besides oil and grease, any paraffin or resin that may have been in the leather, detected by qualitative tests.

5. *Tannins.* The residue from the above is dried and heated with water, filtered, and the aqueous extract evaporated and weighed. In the residue are the tannins and their products, and also glucose, dextrin, and soluble salts used to weight the leather. A portion is incinerated, the ash being the soluble mineral salts, to be examined qualitatively for sulfuric acid, chlorine, and certain metals. The remainder of the residue is powdered and exhausted with cold water, and the tannin and coloring matter precipitated by magnesia and lead carbonate; the filtrate is tested for glucose and dextrin by Fehlings solution; this reagent however will throw down some precipitate from all extracts.

6. *Nitrogen.* The total nitrogen of the leather is determined by one of the usual methods and calculated to dry ash-free leather.

7. *Hide-substance.* From the nitrogen found in (6) the amount of pure hide-substance H may be calculated from the equation $H = \frac{L.Nl}{Nb}$, where L is the dry ash-free leather substance; Nl, the nitrogen in L; and Nb, the nitrogen in the dry, ash-free hide as prepared for tanning, the percentage of nitrogen being fairly constant for any one kind of hide. Deducting H from the pure leather gives the combined tannin. It is said that a complete tannage is realized only where the hide substance has combined with its own weight of tannin.

(The equation is founded on the absence of nitrogen in tannin and like bodies. When a hide is tanned a certain proportion of the tannin, etc., of the liquor enters it and the nitrogen content is proportionately reduced. Hence the proportion —

Per cent of nitrogen in dry, ash-free hide substance : per cent of nitrogen in the same after tanning : : per cent of dry, ash-free leather : per cent of dry, ash-free hide substance in the leather — that is, $Nb : Nl :: L : H$).

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* Proctor Text-book of Tanning; Journ. Socy. Chem. Ind. 1898-164.

THE CARBOHYDRATES.

The carbohydrates are a class of organic bodies composed of carbon, hydrogen and oxygen, the two latter being in the atomic ratio of two to one. They may be divided in three groups.

1. The glucoses, comprising the sugars containing from three to nine atoms of carbon in the molecule. The most common of the members is dextrose, $C_6H_{12}O_6.aq$.

2. The saccharoses, sugars of the formulae $C_{12}H_{22}O_{11}$ and $C_{18}H_{32}O_{16}$. The best known member is cane sugar, $C_{12}H_{22}O_{11}$.

3. The starches and isomers, comprising the starches, celluloses, dextrin, inulin, glycogen, and the natural gums.

The saccharoids are non-fermentable saccharine bodies whose hydrogen and oxygen atoms are not in the water-ratio; mannite, $C_6H_{14}O_6$, is a typical member.

The Sugars.

The most familiar of this family are sucrose, from the sugar cane, white beet and sorgo; dextrose from fruits or made artificially by the hydrolysis of starch; and the sugar of milk. Other sugars, derived from vegetable or animal sources, are of less practical importance. Most varieties of sugar are crystalline and anhydrous, and all are soluble in water.

Sucrose (saccharose, cane-sugar, saccharon), $C_{12}H_{22}O_{11}$. The process of manufacture is essentially the expression of the juice of the sugar cane or white beet, clarification by chalk or lime, decolorization by bone-black, and crystallization. Commercial white sugar is nearly pure sucrose; so rare is adulteration that it is claimed that the ordinary granulated white sugar is the purest manufactured food substance of commerce. Brown sugars, unrefined or partly refined, contain considerable water, glucose, albuminoid and other organic matter, and inorganic salts.

Sucrose crystallizes in rhombic prisms that melt at 160° Cent. and decompose at a higher temperature with the formation of caramel and other bodies. It is freely soluble in water, but insoluble in absolute alcohol; the aqueous solution rotates the plane of a ray of polarized light to the right 73.8° at 20° Cent. Sucrose ferments with yeast giving alcohol and carbonic acid, and when boiled with a dilute acid is transformed to invertose—a mixture of dextrose and levulose. It does not reduce metallic salts in alkaline solution.

Invertose, $C_6H_{12}O_6$, is found in many fresh fruits. It is uncrystallizable and differs from sucrose in that the solution reduces certain metallic salts to lower oxides or to the metallic state, and in having a left-handed rotation for polarized light of 26°. It is fermentable by yeast.

Dextrose, $C_6H_{12}O_6$. Found in honey and many fruits, and extensively manufactured by the hydrolysis of starch by dilute sulfuric acid. It is less soluble in cold water and less sweet than sucrose, reduces metallic salts and rotates polarized light 53° to the right.

Levulose, $C_6H_{12}O_6$. Found in honey and many fruits and can be made artificially by the hydrolysis of inulin. It is uncrystallizable and rotates polarized light—93.7°. It reduces metallic salts.

Milk sugar, $C_{12}H_{22}O_{11}.H_2O$. Crystallizes in four-sided prisms, is less soluble in water than sucrose, reduces metallic salts, and has a dextro-rotation of polarized light of 52.5°.

Maltose, $C_{12}H_{22}O_{11}.H_2O$. Formed in the action of malt infusion on starch. Crystallizes in hard white crusts of fine needles, and is much less soluble in water than dextrose. It is fermentable and reduces metallic salts. Has a dextro-rotation of 135.3°.

Raffinose, $C_{18}H_{32}O_{16}$. Occurs in molasses from beet root sugar, and in manna, barley, etc. Crystallizes in long needles and is readily soluble in cold methyl alcohol. On hydrolysis it is converted into dextrose, levulose and galactose.

From sugar cane the juices can be expressed by a small roller-mill. Sugar beets are rasped or drilled and the sugar extracted from the resulting pulp by water or alcohol, diffusion taking place through the cell walls quite rapidly provided the pulp is sufficiently comminuted. Another plan is to dry the pulp and extract the sugar in a Soxhlet apparatus by hot water or dilute alcohol. A simple method yielding an extract ready for polarization, is that of heating the pulp in a closed flask with water and a little lead acetate and sufficient calcium carbonate to neutralize any free organic acids.

Having obtained evidence of the presence of a sugar in a solution, it may be isolated by precipitating the albumenoid bodies by heating, the dextrin and gummy matters by alcohol, and the organic acids, tannin, etc., by lead acetate. The excess of lead is removed by hydrogen sulfide, and the filtered solution concentrated; on evaporation to dryness, the sugar crystallizes or is left as an amorphous mass according to the variety. A sugar can be separated from colloidal associates by the process of dialysis, but the operation is slow and tedious ordinarily, though it may be considerably shortened by special appliances.

The crystalline or amorphous residue is then to be identified by the action toward polarized light, reduction of metallic salts, susceptibility to fermentation, and other tests.

The principal methods for the determination of sugar are as follows: —

1. From the specific gravity of the solution. When in a clear aqueous solution, free or nearly so from other dissolved matter, the proportion of a sugar may be found from the density, observed by one of the customary methods. With proper care this plan is quite as accurate as that of evaporating the solution and weighing the residue. Perrier states that at a constant temperature and volume each gram of saccharose in aqueous solution increases the densimetric expression by a constant value up to a concentration of forty-five per cent of saccharose; above forty-five per cent the increase is less regular. Tables of the relation between the specific gravity and concentration of solutions of sucrose have been compiled by Balling, Scheibler, Gerlach, and others and will be found in most books of chemical tables and works on sugar analysis.

2. By fermentation. On digestion with a ferment most of the sugars are broken up, the major products being alcohol and carbonic acid, *e. g.*, $C_{12}H_{22}O_{11} + H_2O = 4C_2H_6O + 4CO_2$. Under certain conditions the products are practically constant in proportion to the sugar and may be used as a means of its determination. During the fermentation free oxygen must be excluded, and an ample time allowed for the decomposition, longer for saccharose than for maltose and dextrose. The most suitable concentration for the sugar solution

is said to be about eight per cent, and the temperature of digestion 85°. Sucrose yields about 49 per cent of carbon dioxide and dextrose about 46.5 per cent.

Of the two products, carbon dioxide is the one usually determined as it offers fewer manipulative difficulties than the alcohol. One form of apparatus is shown in Fig. 178. A flask A contains the sugar solution and a small amount of a saccharomycete of a rapidly diffusive variety. The flask is topped by a cork bearing two glass tubes, one B closed by a short rubber tube and a glass rod, the other D joined to an absorption flask E containing a clear solution of barium hydrate, protected from contact with the external air by a Bunsen valve F or other arrangement. The apparatus is kept in a warm place until the fermentation is over — usually from 24 to 48 hours — the carbon dioxide passing into the barium hydrate precipitating an equivalent of barium carbonate. The tube B is pushed down into the liquid and what remains of the gas in the generating flask is expelled by heating the solution and passing a current of pure air. The precipitate barium carbonate is then collected and weighed as usual. It is always best to accompany the analysis by another on about the same weight of pure sugar, since in practice the reaction never proceeds exactly according to the above simple equation.

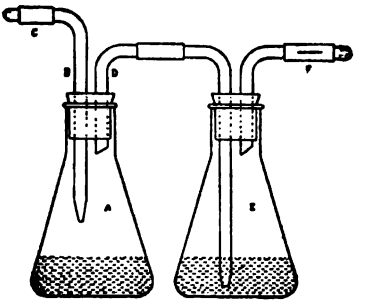

Fig. 178.

Other methods for the determination of the carbon dioxide may be followed, or the alcohol formed may be distilled and determined in the distillate by specific gravity or other process.

3. By polarization. A solution of a sugar rotates the plane of a ray of polarized light to an extent determined by (1), the kind of sugar; (2), the concentration of the solution; (3), the length of the solution traversed by the ray; and (4), the temperature of the solution. Sucrose, dextrose, milk-sugar, and maltose turn the plane to the right (dextrogyrate), while levulose and invertose turn it to the left (laevogyrate).

The specific rotatory powers of the different sugars are stated by Landoldt as follows, the concentration ten grams in 100 Cc. of water, the temperature 20° Cent., and the light the D or sodium ray.

Sucrose	+ 66.58°.	Levulose	— 70.47°.
Milk sugar	+ 52.53°.	Invertose	— 20.02°.
Maltose	+ 138.10°.	Raffinose	+ 104.50°.
Dextrose	+ 52.74°.		

The sugars derived from natural sources are either dextro- or laevo-rotatory, but the same varieties formed artificially may consist of molecules of both right and left-handed rotation. The syrups prepared by dissolving some of the sugars in cold water exhibit an abnormally high or low rotation, coming to the normal after standing for a time, or immediately on heating to the boiling point.

The influence of the temperature of the sugar solution on the saccharimeter reading is not of practical importance within the usual range of laboratory temperatures except for levulose and invertose. Each degree Centigrade of rise in the temperature of a solution of 14 grams of levulose in 100 Cc. of water reduces the angular deviation by .172°; this peculiarity is applied in the analysis of mixed sugars.

The solution of sugar to be polarized must be perfectly clear and quite or nearly colorless, and be free from albuminous and like bodies that have also a rotatory power. Several reagents are in use for clarifying and decolorizing the solutions and precipitating foreign matters that interfere. Basic lead acetate precipitates most organic acids and the precipitate carries down colloidal bodies and coloring matters. Gill states that the excess of the reagent affects the rotatory power of levulose, but that the error can be overcome by certain precautions. Edson recommends normal lead acetate as having some advantages over the basic acetate. In all cases only a slight excess should be used.

Bone-black is an eminent decolorizing agent but should be employed with caution, using as little as will accomplish the clarification, as it adsorbs a small amount of sugar. It has been proposed to percolate the syrup through a column of bone-black, avoiding the error due to retention of sugar by rejecting the first issue of the percolate. Aluminum hydrate suspended in water acts chiefly or entirely in a mechanical way, and alone is suited only for the purer syrups. Acid mercuric nitrate has a coagulating action and is preferable for syrups containing much albuminous matter.

The saccharimeter and its operation are described on page 165.

4. By reduction of metallic salts. Fehlings solution. When an alkaline solution of a cupric salt is boiled with a solution of a sugar mutual decomposition takes place. The exact nature of the reaction is not known, but in general on the one hand the cupric salt is reduced and cuprous oxide (Cu_2O) separates (unless retained in solution by certian reagents), and on the other the sugar is oxidized by the cupric salt and alkali to form oxalic, formic, lactic and other acids and decomposition products. As the reaction proceeds the deep blue color of the copper solution gradually lightens as the copper passes to the cuprous state, until, if the sugar is in excess, the solution becomes light yellow, colored only by the decomposition products or impurities of the sugar. Under certain uniform conditions, *i. e.*, when the reagent is of a given composition and is in large excess throughout the reaction, the sugar solution of a certain approximate concentration, and the rate of mixing the two, and the initial and subsequent temperatures concordant, the reactions between the copper salt, sugar and alkali are practically regular, and the weight of the precipitated cuprous oxide bears a definite relation to the weight of the sugar. But it must be remembered that each variety of sugar has its own specific reducing coefficient and that many other organic bodies react in a similar way.

Of the common sugars, glucose, milk sugar, and maltose reduce Fehlings solution, though in different ratios, while sucrose has no action on it and can only be determined after conversion to invertose.

The typical Fehlings solution is compounded of copper sulfate, sodium hydrate, and potassium tartrate, all dissolved in water. The object of the tartrate is to hold in solution the copper which would otherwise be precipitated as cupric hydrate by the alkali. The tartrate may be replaced by other compounds that contain the hydroxyl group, such as glycerol, mannite, etc.

Many recipes have been published for compounding the solution, modifying the original proportions of the reagents directed by Fehling. In that of O'Sullivan below, the copper sulfate and alkali-tartrate solutions are made up separately and only united just before using, since the mixture slowly decomposes on keeping.

Fehlings solution.

A.

Crystallized cupric sulfate, powdered	69.278 grams.
Sulfuric acid, concentrated	One Cc.
Dissolve in water and make up to	One liter.

B.

Potassium sodium tartrate, crystallized	356 grams.
Sodium hydroxide	100 grams.
Dissolve in water and make up to	One liter.

Equal volumes of A and B are mixed for the determination.

The modification of the original solution due to Rossel substitutes glycerol for the tartaric acid on the grounds that a more stable solution results. In Soldaini's solution no organic matter is contained; it is made up of a solution of the carbonate and hydrate of copper in potassium carbonate. The superiority asserted is the lessened action of the reagent on any cane- or other non-reacting sugar that may be present. For small amounts of invert sugar in sucrose an addition of potassium sulfate is made, the amount of sugar solution added is greater, and the time of boiling reduced.

Since the reaction is greatly modified by the conditions of the experiment, arbitrary directions must be closely followed. Those of Defren are substantially as follows.

The sugar solution is clarified and other reacting bodies removed by lead acetate, or other reagent, and the excess of lead by potassium sulfate. After filtering, the solution is diluted until there is contained approximately one-half of one per cent of sugar, the volume observed, and the solution filled into a burette. Of the copper and potassium tartrate solutions *supra*, 15 Cc. of each are mixed, diluted with 50 Cc. of freshly-boiled distilled water, and heated on the water-bath for five minutes. Twenty-five Cc. of the sugar solution is run into the hot mixture, and the whole kept in the water-bath for 12 to 15 minutes. The mixture at first turns green, then brownish, and finally dingy red. It is filtered by suction and the cuprous oxide washed by hot water until the washings are no longer alkaline. The precipitate is ignited and weighed as cupric oxide and the weight of sugar calculated from the equations below, w being the weight of cupric oxide.

$$\text{Weight of dextrose} = w\,(.4400 + .000037\,w)$$
$$\text{Weight of maltose} = w\,(.7215 + .000061\,w)$$
$$\text{Weight of lactose} = w\,(.6270 + .000053\,w)$$

The weight of the precipitate of cuprous oxide can be found by several plans. A resumé may be of interest.

1. The filter, with the precipitate inclosed, may be burned in an open crucible, and the residue ignited until all the cuprous oxide has become cupric oxide, which is weighed. With the small amounts of precipitate usually obtained oxidation is complete after a short ignition.

2. The precipitate may be caught on a tared paper or a Gooch crucible, and after drying at 100°, weighed as cuprous oxide. It is said that as it is impossible to free the filter from the last traces of the filtrate by washing with water alone, a double filter should be used, the outer paper having been trimmed to an equal weight to that of the inner; this on the supposition that each will retain the same amount of the filtrate. As one paper may not retain the finely divided precipitate it is advised to use a quadruple filter, the two outer counterbalanced by the two inner.

On igniting the precipitate in hydrogen, the vapor of formic acid, or other reducing gas, there is left metallic copper. Here the filtration is done through a thin tube of hard glass of the shape of a calcium chloride drying tube Fig. 158, plugged with asbestos and glass-wool. After drying and weighing the tube, the filtration is proceeded with, the precipitate washed with water, then with alcohol and ether, and the contents dried by conducting a current of air through the tube for a short time. Then the tube is connected to a hydrogen generator and heated moderately; a short exposure effects the reduction to the metal. The tube is cooled while the gas still passes, and is ready for weighing.

3. The cuprous oxide may be dissolved in nitric acid and the copper precipitated electrolytically. Although consuming more time than the other methods, it has several advantages and is preferred by many chemists.

4. Ehrmann would stir the washed oxide into a concentrated solution of sodium platinic chloride, the cuprous oxide decomposing this compound with deposition of metallic platinum which is filtered off and weighed. Superior accuracy has been claimed over the method of reducing the cuprous oxide to metallic copper and weighing, by reason of the higher weight of platinum, though if the equation $Na_2PtCl_6 + 2Cu_2O + 4HCl = 2Cu_2Cl_4 + Pt + 2NaCl + 2H_2O$ is correct, a less weight will be obtained.

5. Similarly Gedult directs to stir the precipitate into an ammoniacal solution of silver chloride — $2AgCl + Cu_2O = Ag_2 + CuO + CuCl_2$ — the cupric oxide formed is held in solution by the ammonia. The deposited silver is filtered off and weighed.

6. More rapid is the volumetric method of Sidersky who dissolves the cuprous oxide in a known volume of standard sulfuric acid and a slight excess of potassium chlorate —

$$6Cu_2O + 12H_2SO_4 + 2KClO_3 = K_2SO_4 + 11CuSO_4 + CuCl_2 + 12H_2O$$

— after which the unneutralized acids (sulfuric and chloric) are titrated by standard alkali.

7. In another volumetric method the precipitate is dissolved in an acid solution of ferric sulfate and the ferrous sulfate formed — $Cu_2O + Fe_2(SO_4)_3 + H_2SO_4 = 2FeSO_4 + 2CuSO_4 + H_2O$ — titrated by standard potassium permanganate.

8. Politis accurately measures the volume of the copper solution boiled with the sugar, and determines, not the weight of cuprous oxide precipitated, but that of the copper remaining in solution. After filtering and washing the precipitate, the filtrate and washings is mixed with potassium iodide ($Cu_2Cl_4 + 4KI = Cu_2I_2 + 4KCl + I_2$), and the iodine set free is titrated by potassium thiosulfate and starch-paste. Instead of filtering, the solution after precipitation may be made up to a definite volume and an aliquot part of the clear liquid withdrawn for testing.

Volumetric methods. The sugar solution is diluted to a definite volume so chosen that the sugar shall be at a concentration of one to two per cent, and a burette filled with it. Beneath is placed a porcelain dish supported over a Bunsen burner. An accurately measured volume of Fehlings solution is run into the dish and heated to boiling. The sugar solution is run in slowly until the blue color nearly disappears, then the titration cautiously continued until a small filtered portion shows no coloration with a solution of potassium ferrocyanide acidulated with acetic acid. If lead acetate has been used for clarification the lead must be removed before the titration since it interferes with the end-reaction.

The formulae for compounding Fehlings solution aim to secure a standard solution of which one cubic centimeter reacts with a definite weight of sugar—usually one milligram. But as the reaction is complex, varying with the conditions of the test, and as in the titration each successive addition of sugar encounters a solution weaker in copper, the reaction slackens continually, and it is evident that a parallel determination on as pure a sugar as can be obtained is to be preferred to a reliance on the equivalent of the solution or a computation from a formula. This also applies to the tables of equivalents of the different sugars for given volumes of Fehlings solution.*

According to Soxhlet, .500 gram of sugar in a one per cent solution reduces the following volumes of undiluted Fehlings solution—

Dextrose	105.2 Cc.	Galactose	98.0 Cc.
Invertose	101.2 Cc.	Levulose	97.2 Cc.
Milk sugar	74.0 Cc.	Maltose	64.2 Cc.

Pavy combines ammonia with the fixed alkali of Fehlings solution by adding ammonia until strongly ammoniacal. With this solution the cuprous tartrate is reduced by the sugar solution to form soluble cuprous ammonium tartrate, and the solution remains clear throughout the boiling, the blue color fading as the copper passes to the cuprous state. Since a hot solution of a cuprous salt is readily oxidized by the air, the titrate is held in a flask whose cork is pierced by the burette tip, and also by a glass tube which leads the steam and ammonia vapors out of the flask into a dilute acid in order that the operator may not be inconvenienced; a Bunsen valve prevents any regurgitation should the titrate become cooled momentarily. A simpler plan is that of Allen who blankets the titrate with a layer of paraffin oil.

Instead of ammonia, Causse would compound potassium ferrocyanide with Fehling's solution, believing that this reagent, while answering the purpose of ammonia, has less action on sugar and its associates.

Allen and Gaud's solution is simply copper sulfate dissolved in an excess of ammonia; while Gerrard holds up the cuprous oxide by potassium cyanide. When using the latter the end-point (the disappearance of the blue color) must not be overstepped, since any excess of the sugar solution produces a green tint.

Knapp's solution. Mercuric cyanide in alkaline solution is reduced by sugars with the formation of a precipitate of metallic mercury. The hot one per cent solution of the salt is titrated by the dilute sugar solution until a drop of the mixture gives no cloud with a drop of stannous chloride, or shows no decided brown tint when exposed to the fumes of ammonium sulfide. Sacchse prefers an alkaline solution of mercuric potassium iodide, using a solution of stannous potassium chloride for an indicator, applied as above. These two solutions are useful in special determinations and in qualitative tests, but for general work, Fehling has the preference. The following table shows the relative action of different sugars on Fehlings (undiluted), Knapps and Sacchses solutions, taking dextrose as 100 for a basis.

	Fehling.	Knapp.	Sacchse.
Dextrose	100.	100.	100.
Invertose	96.2	99.0	124.5
Levulose	92.4	102.2	148.6
Milk sugar	70.8	64.9	70.9
Galactose	93.2	83.0	74.8
Milk sugar, invert	96.2	90.0	85.5
Maltose	61.0	63.8	65.0

* Chem. News, 1894—1—233; Journ. Anal. Chem. 4—329.

4. By precipitation. Reducing sugars from crystalline precipitates with phenylhydrazine ($C_6H_8N_2O_3$), which are termed osazones; usually a designation of the sugar is prefixed, thus glucosazone, lactosazone, maltosazone. One molecule of the reagent unites with one molecule of a sugar to form a normal hydrazone, water being eliminated; but if the phenylhydrazine be in excess, it reacts with the hydrazone to form an osazone, *e. g.*, glucosazone, $CH_2.OH(CH.OH)_3.C.CH : N_2.(NH.C_6H_5)_2$. The melting points of the products of the various sugars differ considerably, ranging from 160° to 205°.

The sugar solution is moderately heated with an excess of an acetic acid solution of phenylhydrazine, the compound falling as a crystalline precipitate, but slightly soluble in water though readily in alcohol. After washing with water the precipitate is dried and weighed. The results are rather low from the solubility of the precipitate.

Carbohydrates, with the exception of the pentoses, when macerated and distilled with a dilute mineral acid, develop furfurol, a volatile aldehyd of the composition $C_4H_3O.COH$. The sugar solution is mixed with dilute hydrochloric acid and distilled until all of the furfurol produced has come over (accompanied by weak acid) as shown by a test with sodium acetate which strikes with it a red color. The furfurol may then be precipitated by stirring with phenylhydrazine, the two reacting to form a crystalline precipitate of furfurolhydrazone. The precipitate may be dried at 60° and weighed, or dissolved in alcohol, the solution evaporated to dryness, dried and weighed.*

Or the furfurol may be titrated by the same reagent in standard solution, using anilin acetate for an indicator.

Phlorglucin produces with furfurol in acid solution a cherry-red color, the liquid showing a characteristic absorption band in the spectrum.† After a short time a brown precipitate falls which has the composition $C_{16}H_{12}O_6$. The precipitate can be collected, washed with water, dried and weighed. Since it is somewhat soluble in water a correction is made for the amount retained in solution.

Some varieties of sugar form definite compounds with certain metals, notably lead and those of the earths. The solubility of such precipitates, however, prevents any extended application of these reactions to quantitative work though a separation from other organic bodies may sometimes be accomplished with passable results. The sugar may be regenerated by suspending the precipitate in water and passing a current of hydrogen sulfide or carbon dioxide to precipitate the base.

Inversion. A notable property of sucrose and some other sugars is that of becoming hydrolyzed or 'inverted' by the action of dilute acids or other reagents. The inversion is far more prompt on heating, and results in the division of the sucrose into a mixture of equal parts of dextrose and levulose, thus

$$C_{12}H_{22}O_{11} \text{ (sucrose)} + H_2O = C_6H_{12}O_6 \text{ (dextrose)} + C_6H_{12}O_6 \text{ (levulose)}.$$

342 parts of sucrose giving 360 parts of the mixture called 'invertose.' The levulose of the mixture however differs somewhat in its properties from levulose derived from natural sources. The inversion of milk sugar produces dextrose and galactose; of maltose gives sucro-dextrose; and of melitose gives dextrose and eucalyn.

The acid takes no direct part in the reaction, acting only as an excitant. Since at ordinary temperatures levulose has the greater rotatory power, the in-

* Journ. Anal. Chem. 1893—190.

† Berichte, 1896—1202.

vertose is laevo-rotatory, but as the temperature is increased the rotations become more nearly equal until at about 88° Cent. they are identical and the invertose shows no action toward polarized light.

Inversion is a great aid in sugar analysis since it supplies two definite, correlated values and gives data for the elimination of the effect of certain optically active associated bodies whose rotation is not affected by heating with acid. The same applies to determinations by means of Fehlings solution on which sucrose has no action.

The reaction given above expresses essentially the change wrought in inversion, but secondary reactions always occur. For this reason it is necessary to follow a certain routine to obtain corresponding results in analysis. The strength of the sugar solution, time and temperature of heating, and other factors modify the yield of invertose to a considerable extent. The directions of Clerget are substantially as follows.

The normal weight of sugar used for the saccharimeter reading (here 16.471 grams) is dissolved and made up with water to 100 Cc., then with strong hydrochloric acid to 110 Cc. The liquid is heated to 68° Cent., so adjusting the source of heat that the thermometer shall attain this temperature in fifteen minutes. The liquid is then cooled rapidly to the temperature of the room, filtered if necessary, and polarized, adding ten per cent to the reading to compensate for the volume of acid. The percentage of sucrose originally present is found from the proportion $S : 100 :$: the algebraic difference between the two readings : the theoretical difference $- .5\,t$; here S is the percentage of sucrose; $t°$, the temperature of the polarized liquid; and the theoretical difference is taken to be either 144° or more usually 142.4°. These figures are derived from the fact that a normal weight of pure sucrose in the standard volume of water reads on the sugar-scale saccharimeter 100° to the right, and after inversion, 44° or 42.4° (according to conditions) to the left; both at a temperature of zero.

The same method is pursued when the invertose is to be determined by means of Fehlings solution, neutralizing the acid before the test.

Although dilute hydrochloric acid is the usual hydrolyzing agent some prefer zinc with hydrochloric acid, stannous chloride, etc. The action of yeast is slower than that of acid but it has some advantages. O'Sullivan* directs that with 50 Cc. of the neutral syrup there be incorporated of brewers yeast about one-tenth of the weight of the sugar, and the mixture heated on the water-bath for four hours; then cooled to 15.5°, clarified by alumina, and diluted to 100 Cc. A portion of the solution is polarized at once, and another portion after several hours have elapsed to ascertain if the conversion was complete in the first instance. Invertase is in some respects superior for the purpose to yeast.

Sucrose is also slowly inverted by many organic and inorganic salts. The rate of inversion may be expressed by the formula $K = \frac{1}{t} \log. \frac{A}{A-x}$ where A is the amount of sugar originally present; x that inverted up to any time t as measured by the difference in rotation; and K, the constant or coefficient of inversion.†

Separation of sugars and impurities. 1. By lixiviation. Cane sugars and the better grades of beet sugars may be assayed on the principle that sucrose

* Journ. Chem. Socy. 57—834.

† Journ. Amer. Chem. Socy. 1896—120 and 693.

is completely insoluble in a mixture of anhydrous alcohol and ether, and in dilute alcohol that has been previously saturated with sucrose. Four solutions are prepared: (A) alcohol of 80 per cent, containing five per cent of acetic acid: (B) alcohol of 88 per cent; (C) alcohol of 94 per cent; and (D) absolute alcohol mixed with half its volume of anhydrous ether. The first three are saturated with sucrose by digestion over the crystals for several days at the normal temperature of the laboratory.

A certain weight of the dried sugar is placed in a long tube similar to a Mohr's burette, and percolated successively with the four solutions, avoiding any decrease or increase in the temperature of the first three which might precipitate some of the sucrose they hold, or cause them to dissolve some of the sucrose of the sample. The pure crystallized sugar remaining is then dried and weighed, or dissolved and polarized.

Casamajor, reversing this process, determines any starch sugar that may be in commercial cane sugar by extracting the dried sample several times with a saturated solution of starch-sugar in methyl alcohol. The residual glucose is washed rapidly with pure methyl alcohol, dried and weighed.

2. If to a mixture of sucrose and a reducing sugar there be added a limited proportion of lead protoxide, the reducing sugar preferentially unites with it, and where the proportions of the two sugars are approximately known a fair separation is possible.

To a mixture of sucrose, invertose, and dextrose or levulose, Winter adds ammoniacal lead acetate and dilutes largely. All three sugars form compounds with lead oxide, but only the sucrose-lead compound is freely soluble and passes into the filtrate; the sucrose can be regenerated by transmitting a current of carbon dioxide which precipitates the lead as carbonate and leaves the sucrose in solution to be determined by the usual methods. The precipitate of the lead compounds of invertose and dextrose or levulose is suspended in water and treated with carbon dioxide which decomposes the dextrose-lead compound only, giving on filtration a solution of dextrose and a residue of lead carbonate plus the lead-levulose compound. The latter is suspended in water and a current of hydrogen sulfide passed, when all the lead becomes sulfide while the levulose enters into solution. The separation is only fair at best.

3. But in most cases no direct separation is attempted. Indirect methods are based largely on calculations from the variation of the constants of polarization, reducing power toward metallic salts, etc., determined on the sample intact and also after some physical or chemical change has been wrought. A few examples are appended.

A. Given a mixture of only sucrose and optically inactive matter. A saccharimeter weight (26.048 or 16.471 grams) is dissolved and polarized, reading a divisions on the sugar-scale, the percentage of sucrose.

If another equal weight were dissolved, inverted by acid, and polarized, the reading would be b divisions; were the sample entirely sucrose, a would be $100°$, and b, $-42.4°$; that is, the divergence would be $K = 142.4°$ at zero Cent., and at any higher temperature $t°$, would be $K - .5\ t$. But as sucrose formed only part of the sample, the percentage shown directly by a, b lessens as the ratio of a to 100 diminishes.

B. A mixture of sucrose and dextrose. Proceeding as above, the percentage of sucrose $S = \frac{100\,(a-b)}{K}$ and of dextrose $D = \frac{100\,c}{3.055\,A}$.

In this case the reading a is the sum of the (right-handed) rotations of the two sugars, and after inversion, the reading b is the left-handed rotation of invertose diminished by the right-handed of the dextrose; in other words,

each reading is affected by the same quantity c, the rotation due to dextrose. Hence if the percentage of sucrose in the mixture by represented by S; the reading before inversion by a and after inversion by b; the rotatory power of the dextrose by c; and the divergence of sucrose and invertose by K; then $S : 100 :: (a-c)-(b-c) : K$; whence $S = \frac{100\,(a-b)}{K}$.

The first polarization minus the percentage of sucrose equals the rotatory power of the dextrose expressed in degrees of the sugar-scale, that is, $a - S = c$, for if the sample contained 100 per cent of sucrose the rotation would be 100, hence a sample containing S per cent will read S divisions.

One gram of dextrose is equivalent to 3.055° on the sugar-scale, therefore the weight of dextrose d for a deviation c is given by the proportion $3.055 : c :: 1 : d$; and since the weight A of the sample was polarized, the percentage of dextrose D is found from the proportion $A : d :: 100 : D$; whence $D = \frac{100}{A} \times \frac{c}{3.055}$.

The same method can be applied to mixtures of sucrose with other sugars whose gyrodynat is not changed in the process of inversion.

C. A mixture of sucrose and invertose may be analyzed by polarizing at a moderate temperature and again at 87.6° at which point invertose has no rotatory power. The calculation is simple. Or the mixture may be boiled with Fehlings solution which is decomposed by the invertose only, then another portion inverted, neutralized, and determined as before; the difference in the weights of cuprous oxide is that corresponding to the invertose from the sucrose.

D. For a mixture of dextrose and maltose, Sieben determines the total reducing power of the mixture toward Fehlings solution, then the reducing power toward an acetic acid solution of cupric acetate from which only dextrose precipitates cuprous oxide, maltose not being decomposed by this reagent.

E. If a mixture of cane and milk sugars be boiled with a two per cent solution of citric acid, only the former will be inverted; another reagent for the purpose is benzoic sulfinide.

F. For sucrose, dextrose and levulose, Sieben has proposed a method based on these principles: sucrose does not precipitate Fehlings solution as do dextrose and levulose; sucrose is converted into equal parts of dextrose and levulose by inversion; and levulose is destroyed on heating with hydrochloric acid of a strength that will invert sucrose. In practice the dextrose plus levulose are first determined by Fehlings solution; then the sucrose is inverted and the total reducing sugars found in the same way, and also by polarization; and finally, the levulose is destroyed by long heating with hydrochloric acid of a particular strength, and the remaining dextrose is determined by Fehlings solution. These data are sufficient for computing the proportions of each sugar, but that the levulose can be eliminated without some change taking place in the dextrose is very questionable.*

G. The determinations of a mixture of dextrose and invertose may be accomplished by calculation from the unlike action of Fehlings and Sacchses solutions (page 433) on these sugars. If a represents the volume of Fehlings solution reduced by one gram of dextrose; a', that reduced by one gram of invertose; and d, that reduced by a given volume of the solution of the two sugars; and if b, b', and d' represent the corresponding figures for Sacchses solution; and x

* Journ. Anal. Appl. Chem. 5—401.

and y the weights of dextrose and invertose respectively in the given volume of the sugar solution: then $d = a\,x + a'\,y$, and $d' = b\,x + b'\,y$; whence $x = \frac{a'd - b'd}{a'b - a'b}$

The analysis of a commercial raw or refined sugar is made on the following lines.

1. Determination of water. On account of the ready decomposability of the sugars the heat is limited to 75° or 80°. In the case of syrups it is better to soak up a suitable weight of the sample, diluted if quite viscous, in a porous medium such as sand, blotting paper, or the like.

At best this conventional method is tedious and uncertain from the unstable and easily oxidizable nature of sugar, and it has been found by tests on pure sugar, weighed, moistened and dried, that desiccation in vacuo leaves much more nearly the original weight of the sugar than if under atmospheric pressure. Thorne and Jeffers* describe an apparatus in which the weighed sugar is distributed in a coil of filter paper by means of a little water; the roll is dried in a slow current of highly rarified dry carbon dioxide at a heat of from 65° to 70° furnished by a bath of the vapor of boiling methyl alcohol. About six to ten hours drying is needed. They find that both the prescribed temperature and the atmosphere of rarified carbon dioxide are essential to correct results.

2. Determination of the inorganic constituents. These are principally the fixed alkalies and earths combined as organic salts, but may also be in part sand, clay, etc. On incineration of the sugar there are formed at first caramel and like bodies; at a higher heat a carbonaceous mass remains, this finally burning to an ash composed largely of carbonates of the alkalies resulting from the decomposition of the organic salts. Simple incineration of the sugar is apt to be tedious for the reason that a comparatively low heat must not be exceeded for fear of loss of some of the bases by volatilization. A common practice is to moisten the char with sulfuric acid, dry and ignite in air whereupon the carbon readily burns; there are left sulfates of the bases, and a conventional deduction of ten per cent of its weight is made for the sulfate radical. A more rational procedure is to report the result as so much 'sulfated ash.'†

The char burns more readily when the sugar has been dissolved in a little water and the solution imbibed in a weighed quantity of clean sand. Courtonne recommends ferric oxide for the purpose, but the liability of reduction to a lower oxide on ignition with carbon is against the use of this compound. To render the char porous, Boyer heats the sugar to carmelization in a platinum capsule, adds a solution of benzoic acid in alcohol, and ignites; the vapors from the decomposition of the acid cause the mass to be spongy and easily burned.

Laugler attempts the reproduction of the compounds as they exist in the sugar. The sample is treated with dilute sulfuric acid which discomposes the organic salts and sets free the organic acids thereof, and these are extracted from the syrup by ether. Another equal weight of the sample is burned to an ash, on this poured the ethereal solution, evaporated to dryness, and weighed. The organic acids decompose the carbonates of the ash.

An analysis of the ash is not often asked for; it is made by the usual methods of inorganic analysis.

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* Journ. Socy. Chem. Ind 1898—114.

† School of Mines Quart. Vol. 2, No. 1.

3. Organic acids. These are set free on treating the concentrated solution of the sugar with dilute sulfuric acid, and may be extracted by ether, the ethereal solution mixed with a little water, and titrated by weak standard alkali.

4. The insoluble matter, usually clay or sand, is determined by dissolving the sample in water, filtering, washing with water, drying the residue and weighing.

5. Free acid in appreciable quantity is rarely found; it may be determined by direct titration by weak standard alkali and litmus.

6. The determination of the sucrose and invert sugar is made either by the polariscope or Fehlings solution as before described, first in the aqueous solution, then after inversion, and the results calculated from the usual formulae.

Commercial starch-sugar or glucose is a complex mixture composed mainly of dextrose and maltose, with dextrin, unfermentable carbohydrates, and inorganic matter including a trace of sulfuric acid. It is extensively manufactured by hydrolyzing corn starch or potato starch by dilute sulfuric acid, removing the acid as calcium sulfate by means of chalk, and evaporating to a syrup or to crystallization. There are found in the market two forms, one a thick colorless syrup called "corn syrup" or "confectioners glucose" of a specific gravity of about 1.4 and containing about 23 per cent of water; the other a white granular solid, "grape sugar." Both kinds are largely used in the preparation of the cheaper grades of confectionery, syrups, preserves, etc. The crystallized glucose is mainly dextrose, and is less sweet than cane sugar, the ratio being about 1 to 1.53.

Water is determined in the usual way by drying at 100°; the last traces are removed by moistening with absolute alcohol and redrying. Corn syrup is best dehydrated by diluting with weak alcohol, imbibing the liquid in a weighed quantity of sand, and drying, finally moistening with strong alcohol and redrying.

The *specific gravity* observation presents some difficulties from the viscous nature of the syrup. A fairly accurate method is that of diluting a weighed quantity with water to a known volume and observing the gravity of the solution.

Inorganic matter, chiefly calcium sulfate, generally runs below one per cent, and is left on burning in a platinum dish. To prevent the inconvenient swelling up of the mass on carbonizing, the syrup or concentrated solution may be dropped into a red hot platinum dish (page 105). The presence of calcium sulfate or other calcium compound in the ash differentiates commercial starch-sugar from the sugar from natural sources.

The determination of the other constituents, with perhaps sucrose added during manufacture to augment the sweetness of the product, cannot be made with any assurance that the results are more than fair approximations. It is said that in samples of commercial glucose the relation between the optically active and copper-reducing constituents is a constant and may serve to indicate the nature of the saccharine bodies present.

Possibly the most satisfactory method is to dissolve the sample in a little water and precipitate the dextrin by strong alcohol, then decant the solution and weigh the dextrin and ash. On distilling the alcohol there is left an aqueous solution of dextrose, maltose, carbohydrates and possibly sucrose; it is diluted with water and five aliquot parts withdrawn.

The first is fermented by yeast to destroy all but the unfermentable carbohydrates and these determined by the polariscope; the second is boiled with

Fehlings solution, the cuprous oxide precipitated corresponding to the dextrose and maltose; the third is inverted by acid and boiled with Fehlings solution, the increase in weight of the cuprous oxide over the preceding coming from the inverted sucrose; the fourth is polarized directly; and the fifth after inversion. Knowing the specific rotation of each sugar, the proportions of dextrose and maltose can be deduced by a somewhat complicated calculation.

Another method determines the rotary power $[a]_D$ and the reducing power toward cupric tartrate, K; also the specific gravity and the ash, from which data may be calculated the total organic matter S. Then the percentages of maltose M, of dextrose D, and of dextrin d are found from the formulae

$M = S.\ \frac{[a]_D + 1.42\,K - 195}{27.2}$; $D = \frac{S.K}{100} - .61$; and $d = S - (M + D)$. A correction is to be made for the action of the acid on the dextrin.

The total *nitrogen* is ascertained by the Will-Varrentrapp or the Kjeldahl method or by Nessler's test. The product of the result by the factor 6.25 is the albuminoid matter.

Free acid should not exceed traces, found by titration by weak standard alkali.

Expressed honey is essentially a clear concentrated solution of various sugars, principally dextrose and levulose or invert sugar, together with the saccharoid mannite (a hexatomic alcohol), and small quantities of wax, mineral matter, organic acids, etc. The percentage of water ranges from 15 to 25. It is said that the honey derived from flowers is laevo-gyrate, that from conifers dextro-gyrate, and from both, either indifferent or weakly right or left handed as may be.

The principal adulteration is by admixture of starch sugar, though an entirely factitous article is said to have been manufactured from flavored and slightly tinted glucose, inclosed in cells of paraffin. The analysis follows the lines of that for starch-sugar, the principal tests being designed to detect adulteration with that body.

The ash in genuine honey should not exceed 5 per cent, and if over 3 per cent should be tested for calcium sulfate, absent from genuine honey but an almost invariable concomitant of glucose. A factitious honey made up of dextrose and levulose has been found on the market; as stated by Hehner there was no phosphoric acid in the ash, an invariable constituent of the ash of genuine honey.

The matter insoluble in cold water is tested by iodine for starch, a blue color pointing to the presence of flour. After fermentation with yeast, the residual unfermentable matter, principally carbohydrates, should not exceed 8 per cent. Dextrin from added starch-sugar may be precipitated by strong alcohol, or the honey may be fermented and the dextrin and carbohydrates polarized, then heated with dilute acid and the latter found by Fehlings solution.

STARCH.

The starches are the major constituent of cereals, forming over half their weight. A microscopic examination of the starch from different plants reveals marked peculiarities of structure, and the size of the granules (from .02 to .10 Mm. in diameter) and their configuration, the position and shape of the hilum, and the appearance under polarized light in conjunction with a selenite plate

often afford a clue to the origin of the sample. Muter* divides the starches into five groups differentiated by their microscopic structure, the examination made by a .4-inch objective and B eye-piece, water immersion and oblique illumination; viz.: (1), the potato group; (2), the leguminous starches; (3), the wheat group; (4), the sago group; and (5), the rice group.

To starch is assigned the empirical formula $(C_6H_{10}O_5)n$; the molecular weight is undoubtedly very high. It is composed of two allied bodies, granulose, colored blue by iodine, and pseudo-cellulose, colored pale yellow by this reagent; the two may be separated by dilute chromic acid which dissolves the former only. The blue color struck with iodine by a cold acid solution of granulose is a delicate and characteristic test of starch; the formula of the compound is said to be $(C_{24}H_{40}O_{20}I)_4.HI$.

The starch of commerce is a white, tasteless and odorless powder agglutinated in the form of irregular fragments, containing from 16 to 28 per cent of water, and a little fat, and mineral and nitrogenous matters. It is insoluble in alcohol and ether and in cold water, but in water heated to above 60° the granules swell and burst, and a perfectly colloidal solution results which is highly dextro-rotatory (190° to 200°), but has no reducing action on copper salts. Starch is also soluble in hot glycerol, and in cold hydrochloric acid of 1.2 specific gravity, with some alteration however.

On heating starch to 160° to 200° or for a limited time with a dilute acid or a solution of invertase, it is converted into dextrin (British gum). Dextrin is an isomer of starch and is found in the market as a light yellow amorphous powder. It is of a gummy nature, readily soluble in water, and, like starch, is converted into oxalic acid when heated with nitric acid, a distinction from ordinary gums which form mucic acid. Dextrin gives no blue color with iodine, rotates polarized light to the right 200.4°, does not precipitate metallic salts, and is converted into dextrose by heating with a dilute acid. Its insolubility in alcohol is applied in analysis as a means of separation from sugars, etc., usually by compounding the concentrated aqueous solution with a large volume of alcohol, the dextrin precipitating as a cohesive mass.

Separation. An approximate mechanical separation from gluten, cellulose, etc., can be made by washing the powdered material on a closely woven sieve with cold water; a milky liquid passes through holding the starch granules in suspension and leaving other insoluble constituents on the sieve. The liquid is allowed to settle and the starch collected and determined in the usual way.

Mixtures of starch with sugars or other soluble bodies can be parted by lixiviation with cold water.

Asboth† is the author of a method of separation which under certain conditions is perhaps the most accurate of any. The basis is the formation of a compound of barium oxide and starch of the formula $(C_6H_{10}O_5)_4.BaO$, soluble in water but reprecipitated by alcohol. The starch is obtained in solution by heating with water, and to the clear liquid there are added a measured volume (an excess) of a standard solution of baryta, and alcohol up to a definite volume. When the precipitate has subsided, an aliquot portion of the clear liquid is withdrawn and the residual baryta determined by titration with standard hydrochloric acid. In the analysis of cereals the starch is first freed from fatty matter by ether, the residue rubbed with cold water and the emulsion poured off and treated as above. Spence‡ states that when a volume of 50 Cc. is used

* Allen, Coml. Org. Anal. 1—408.
† Chem. Zeit. 1888—693 and 1889—591.
‡ Journ. Socy. Chem. Ind. 1888—77.

for one gram of starch the baryta solution should not be weaker than about fifth-normal. From numerous criticisms of the method it is probable that it is trustworthy only for certain material and in the hands of practiced operators.

Amylogen, the soluble starch produced by heating the commercial variety in a closed vessel to 100°, is precipitated from its aqueous solution by alcohol, ammonium lead acetate (as $C_{12}H_{18}Pb_2O_{11}$), and several other reagents. Burkhardt states that if alcohol be added to a solution until faint turbidity ensues and the mixture warmed and treated with tannic acid, all the starch will separate on cooling as a flocculent starch-tannic-acid compound; the acid can be removed by washing the precipitate with alcohol.

All the methods for the determination of starch in mixtures without its separation depend on the principle that starch is converted into dextrose by the action of certain excitants. However, this conversion never affords the theoretical amount of dextrose but only 93 to 97 per cent, the remainder being bodies of the nature of dextrin. Concerning the latter it is claimed that but three simple carbohydrates, possibly in molecular aggregates, exist in the solution of a starch product hydrolized by acids.

Rolfe and Defren * from a study of the hydrolysis of starch deduce that the first change is to amylo-dextrin ($C_{36}H_{62}O_{31},H_2O$), then by successive stages through malto-dextrin, maltose and dextrose, ultimately to dextrose entirely. As the conversion proceeds the rotatory power of the product diminishes; thus, taking no account of reversion products, at 195° of the polariscope the dextrin is 100 per cent and the maltose and dextrose none; at 129° the dextrin has decreased to 27.5 per cent, dextrose has been formed to the extent of 28.4 per cent, and maltose to 44.1 per cent, its maximum; and at 53.5°, both dextrin and maltose have disappeared, the dextrose becoming 100 per cent.

The usual amylolytic agent is dilute hydrochloric acid. The starch-bearing substance is simply boiled with a suitable amount of the acid, filtered from insoluble matter, and the dextrose determined by Fehlings solution. But in some cases the results may be highly erroneous since starch-free bodies — *e. g.*, the sheath of the kernels of maize — when treated as above yield copious precipitates of cuprous oxide. The same holds where other acids, as nitric, oxalic, or salicylic, are substituted for hydrochloric; in fact, the investigations of Stone show that the pentosan that occurs in all feed-stuffs behaves exactly as does starch in any of the methods of inversion by acids, and in Asboth's precipitation method as well.

Starch is hydrolyzed when heated with water for several hours at a pressure above atmospheric. Should sugar be present, a trace of tartaric or citric acid is added to prevent its decomposition.

A method in common use is based on the activity of invertase, a ferment which has no effect on the pentosans, a property often of great advantage. As the preparation of invertase itself is a rather tedious process and the product loses its power on keeping, a freshly prepared aqueous extract of malt is usually substituted, answering the purpose though subject to a correction for the starch and sugar it contains; the extract is made by steeping ground malt in water and filtering. Maercker's revised method† directs heating the amyliferous body with water, and after cooling somewhat, with a little of the malt extract. The mixture is acidified by tartaric acid and heated under a pressure of several atmospheres in an autoclave, then cooled and filtered from

* Technology Quarterly, 1897—Mar.

† Zeits. anal. 24—617.

cellulose, etc. In the filtrate the dextrin and maltose are converted to dextrose by boiling with dilute hydrochloric acid. The malt extract is treated in the same way to ascertain the proper deduction for its starch and sugar. Any fat contained in the sample is previously removed by extraction by ether.

Later methods omit the heating in an autoclave. Hibbard * has devised a method similar to the above especially adapted to fodder, cattle foods, and the like. He prepares an extract by soaking malt in water containing from 15 to 20 per cent of alcohol for a preservative. The powdered substance is compounded with water and a little of the extract, and the mixture heated to boiling, then cooled somewhat, more extract added, and again boiled. After cooling, the liquid is tested by iodine solution to detect unconverted starch; if found, the above treatment is repeated. The solution is now filtered through fine muslin and an aliquot part boiled with a small volume of hydrochloric acid in a narrow-necked flask. The solution is cooled, nearly neutralized by sodium hydrate, and the dextrose determined by Fehlings solution with a correction for the malt extract used.

It is said that at any period in the conversion of starch by diastase the product behaves as a mixture simply of maltose and dextrin, and that the rotatory power bears a constant ratio to the cupric reducing power, so that one can be calculated from the other. † Wein's table, revised by Krug, for the weight of starch corresponding to different weights of copper oxide from Fehling's test will be found in the Journ. Amer. Chem. Socy. 1897—452.

Various other ferments induce hydrolysis, such as amylopsin (contained in pancreatic juice) and taka-diastase. Chittenden ‡ has obtained good results with neutralized human saliva, which contains the ferment ptyalin, followed by dilute hydrochloric acid; an advantage over malt extract is that there is needed no correction for starch and sugar contained.

A number of attempts have been made for the colorimetric determination of starch utilizing the intense blue color struck with free iodine, but as yet the exact composition of the starch-iodine compound has not been established. A solution of erythro-dextrin shows a red color with iodine, and one of cellulose a violet tint.

In the analysis of commercial starch made from potatoes, wheat or corn, there are to be determined the water, ash and proteids, and the starch, the latter by one of the methods described or simply by difference. The origin of the sample may be ascertained by a microscopic examination.

Determination of *water*. On account of the facility with which starch is converted into dextrin, the drying is conducted in vacuo or a current of some neutral gas, first at a low heat, finally to near 100°.

Bloch, § for the approximate determination of moisture in commercial samples, has devised a 'feculometer' on the principle that ten grams of pure *dry* potato starch forms when mixed with water a sort of hydrate of a volume of 17.567 Cc., this volume varying inversely with the percentage of water in a sample. The apparatus is a measuring tube, the upper open end expanded to a funnel for introducing the starch and water; the lower part, 22 Cm. long and 16

* Oil, Paint, and Drug Reporter, 1895—24.
† Journ. Amer. Chem. Socy. 1895—587 and 1896—536.
‡ Journ. Anal. Chem. 1888—153.
§ Journ. of Applied Chem. 1874—73.

Mm. internal diameter, is closed at the bottom and marked with a scale graduated in degrees from zero at the bottom to 100° at 17.567 Cc. For a test, ten grams of the powdered starch is washed into the lower tube with cold water and after settling, its height is read on the scale, which equals the percentage of dry starch in the sample. The difference between 100 and the reading is the moisture contained; about 24 per cent is the maximum. If the sample is adulterated or spoiled the hydrate will not readily settle and it cannot be tested in the instrument.

Another method is that of Scheibler.* When starch powder containing 11.4 per cent of moisture is shaken up with alcohol of .8339 sp. gr. (containing 90 per cent of alcohol) the density of the latter remains unchanged, but if the starch contains less than this percentage of moisture water is absorbed from the alcohol and its gravity lowered proportionally, and if containing over 11.4 per cent it gives up water to the alcohol. One hundred Cc. of alcohol of the above strength is mixed with half its weight of starch in powder, the mixture filtered, and the specific gravity of the filtrate observed. A table (loc. cit.) shows the percentage of moisture corresponding to different gravities from .8226 to .8798, a difference of about .0009 being equivalent to one per cent of moisture.

The *ash* is determined by simple ignition in air. It is composed mainly of phosphates of the alkalies and earths, and silica.

The *proteids* are deduced from the nitrogen found by the methods of ultimate analysis.

For practical purposes the *starch* may be estimated by difference closely enough. If it is desired to determine it directly, the sample is heated to 100° with eight to ten times its volume of water containing about .5 gram of hydrochloric acid gas; the digestion is continued for three or four hours. The reaction is assumed to be $C_6H_{10}O_5 + H_2O = C_6H_{12}O_6$, 162 parts of starch producing 180 parts of dextrose. But practically only about 176 parts of dextrose are formed. Guichard boils the sample for several hours (under a reflux condenser to prevent evaporation) with a mixture of one volume of concentrated nitric acid with nine volumes of water. The results by acid inversion are more exact than in the case of more complex bodies, such as the cereals.

MALT.

On exposing barley to moist air in a moderately warm place the grains sprout; during the germination starch is converted to dextrin and glucose, and there is generated a small amount of a peculiar ferment known as diastase.

In the process of malting, the barley is covered with water and allowed to 'spire' until the plumules have reached about one-half inch in length. Then the germination is arrested by 'killing' the grain by heating to 82°; it is then dried at about 55°, sometimes as high as 75° to 80°.

The objects of subjecting the barley to the process of malting are the dissolution of the cellulose forming the cells in which the starch granules are inclosed, and the consequent liberation of the starch; the breaking down of the nitrogen constituents of the corn; and the production of diastase for future service in the mash tub. When the original barley is inferior or the malting has not been carried out on proper lines, the cellulose surrounding the starch granules is not dissolved, and it is hardly possible for the diastase to convert the encysted starch at ordinary temperatures.

The formula of diastase has not as yet been satisfactorily established, but

* Biederman's Chem. Kal. 312.

investigations point to its being a complex body whose activity depends on a principle called maltin. One part of diastase will convert as high as 2000 parts of starch into dextrin and maltose, the latter the chief product. It may be prepared by extracting ground malt with tepid water and heating the wort to about 75° to coagulate albumin, and, after filtering, precipitating the diastase by alcohol in the form of white amphorous flakes. These are washed, first with diluted alcohol then with absolute alcohol, and dried in vacuo at ordinary temperatures.

Omitting the water contained, the following analyses record successive stages in the practice of malting.*

	Barley.	After steeping.	After 14 days steeping.	Dried malt.	Malt dust.
Starch and dextrin	80.42	81.12	70.09	72.03	43.68
Sugars	2.56	1.56	12.14	11.01	11.35
Crude fiber	4.69	5.22	5.03	4.84	9.67
Proteids	9.83	9.83	10.39	9.95	26.90
Ash	2.50	2.27	2.35	2.17	8.40

An analysis of malt is of value to the brewer as indicating the quality, flavor and brilliancy of the beer or ale made from it. Moisture exceeding four or five per cent points to insufficient drying of the malt or improper storage; a low per cent of sugar is evidence that the germination of the barley was prematurely checked, while a high (over 17) percentage argues the sprouting to have been too rapid. To the soluble proteids of the malt used is credited much of the nutritive value of a beer. Unmodified starch ('steeliness') is but slowly and incompletely converted in the routine process of brewing and tends to haze or cloud the beer: it should not exceed 7 per cent. The diastatic power of the wort is a measure of the capacity of the malt to convert starch beyond what is self-contained. From the acidity, which should not be over .7 per cent, may be judged the age of the malt. The percentages of free maltose, malto-dextrins and dextrin determine the condition, flavor and attenuation of the beer when the mashing is done under fixed conditions. Finally, the color indicates the heat of drying and determines to a great extent the color of the beer.

The complete analysis of a malt may be made in the following manner although opinions differ as to which and how many of these determinations are really necessary to fix the quality or selling price.

1. *Moisture.* From four to five grams is weighed in the form of grains and bruised in a mill. After transferring to a watch glass, the heating is done at a temperature of 100° to 105°, best in a current of dry hydrogen, assuming constant weight when the deviation does not exceed .25 per cent. On account of the hygroscopic nature of malt, protection from the air during the weighings is important.

2. The *ash* remains on burning—it is mainly potassium and magnesium phosphates and silica.

3. The *acidity* is determind by extracting the sample with cold water and titrating by a weak standard alkali. The result is calculated to lactic acid.

4. *Extractive matter* is found by a process of mashing. Quite a number of methods have been put forward, differing in details, but all agreeing in the general conduct, namely, the heating of a large weight of the malt with water for a given time at a given temperature, filtering, and determining the matter in

* Journ. Franklin Inst. 1900—198.

solution either from the specific gravity or by evaporating a portion to dryness and weighing the residue. The extract is also used for other determinations.

Jalowetz' method. Fifty grams of salt is ground in a mill, then washed into a weighed beaker of 500 Cc. capacity with 200 Cc. of water at 45° Cent. The beaker is heated in the water-bath for one half hour at 45°. The heat is then increased at the rate of one degree per minute up to 70°, and kept at this point until a drop of the liquid removed to a porcelain plate gives only a weak red or pale yellow color to a drop of iodine solution. The time of heating is termed the "time of saccharizing". The mash is cooled and to it is added 200 Cc. of cold water, and then made up with water to exactly 450 grams. Part of the mash is filtered through a large dry ribbed paper and the specific gravity of the wort found by a picnometer at the temperature of 17.5°. Cent.

The calculation of the extractive matter in the malt is from the following proportion: — the weight of extractive in 100 grams of wort : the weight of water in 100 grams of wort : : weight of extractive in 50 grams of malt : weight of water in the total mash.

Let e represent the grams of extractive in 100 grams of wort as found from the specific gravity of the wort; then $100 - e$ is the grams of water in 100 grams of wort. If the percentage of water in the malt as found by (1) supra is w, then $\frac{w}{2}$ is the grams of water in 50 grams of malt and $400 + \frac{w}{2}$ expresses the total weight of water in the mash. And if E be the percentage of extractive in the malt, then $\frac{E}{2}$ is the grams of extractive in 50 grams of malt. Whence the proportion $e : 100 - e : : \frac{E}{2} : 400 + \frac{w}{2}$; and $E = \frac{800e + ew}{100 - e}$

Heron's method* is in considerable use. Fifty grams of the ground malt is quickly weighed and covered with 400 Cc. of water at 68°; the mixture is kept at 65° to 66° for one hour with occasional stirring. After cooling to 15.5°, the mash is made up to 515 Cc. (the 15 Cc. is an allowance for the volume of the grains), filtered, and the gravity of the filtrate taken at 15.5° Cent. The color and flavor of the wort are noted.

Miller's modification.† Fifty grams of the ground malt in a tared copper beaker is covered with 200 Cc. of water at 40°, and the mixture heated to 60° and kept at that temperature for 20 minutes with constant stirring; then tested by iodine for starch and erythro-dextrin. If a coloration is noted the mash is further heated, not above 70°, until no coloration is shown. After cooling, water is added to the weight of 450 grams plus the tare of the beaker — that is, a total of 400 Cc. of added water. Filtering clear, the percentage of extractive matter in the wort is found from the specific gravity by the tables of Schultze. The percentage of extractive matter in the malt itself should be represented by $\frac{400}{50}$ of that in the wort, but from Miller's experiments he concludes that while this fraction may represent the amount of extract afforded the brewer, yet the absolute amount obtainable is higher — about $\frac{438}{50}$. If, instead of deducing the extractive from the density of the wort, an aliquot part is evaporated, dried, and weighed, the temperature must be restricted to about

* Journ. Socy. Chem. Ind. 7—259.

† Journ. Amer. Chem. Socy. 1894—353.

75°, since a higher temperature will cause decomposition of the maltose and loss in weight.

The extract as obtained from the above is reserved for the following determinations.

5. The *diastatic power* of the extract is gauged by the proportional weight of starch in aqueous solution that it will convert to maltose and dextrin, and the ratio is taken as a basis for an expression of the diastatic capacity. Several methods have been proposed.

One of these follows the lines of Lintner's scheme for the valuation of samples of impure diastase. The directions are to measure out from a solution of the sample of known concentration a number of equal volumes, and to each add ten Cc. of a two per cent solution of pure potato starch and allow the mixtures to ferment. Then to each is added five Cc. of Fehlings solution and the liquid boiled; where sugar has been formed by the action of diastase on starch in excess of what is required to decompose all the Fehlings solution, the supernatant liquid will be yellow, but where less sugar has been formed the excess of copper will color the liquid blue. Intermediate will be found one of the tests that is colorless (or but faintly blue or yellow), showing that starch was inverted in quantity to exactly correspond to five Cc. of Fehlings solution, and from this datum the weight of the starch can be computed. Lintner proposed to designate as 100 the capacity of the most active specimen of diastase he was able to prepare, namely of which .00012 gram hydrolyzed a weight of starch the products just sufficient to combine with five Cc. of Fehlings solution, operating under the above conditions, and the capacities of other specimens by proportional figures.

A simpler method is to slowly add the wort from a burette by single cubic centimeters to a hot mucilage of starch of known concentration. The point where all the starch has been hydrolyzed is found by testing with iodine solution.

An old approximate test is that of digesting two equal weights of bread taken from one loaf, one with a measured portion of the extract, the other with an equal volume of water. After filtering, equal volumes of the filtrates are evaporated, dried, and weighed; the difference, less the weight of extractive matter in the wort, is the amount of bread made soluble.

6. *Maltose* and *dextrose* are determined by Jalowetz in the wort prepared as in (4). Of this 30 Cc. is diluted with water to 200 Cc. and 25 Cc. withdrawn and treated by Fehlings solution. From Wein's tables is found the corresponding sugar $= m$. Then in the 30 Cc. of the wort there are $8\,m$ grams of sugar. Let the weight of the extract in 100 Cc. of the wort be e grams, and the density of the wort d, then the extractive in 30 Cc. or $30\,d$ grams is $\frac{30}{100} d.\,e$. Whence $.3\,d.\,e : 8\,m :: E : M$; or $M = \frac{8\,m.\,E}{.3\,d.\,e}$

The separate determination of the maltose, dextrose and dextrin may be done in several ways. One of these is founded on the right-handed rotation of the three, the copper-reducing power of maltose and dextrose, and their practically complete decomposition on fermentation by yeast, the dextrin being unaffected. Assuming that the dextrogynat of the dextrins is 193, of dextrose 53, and of maltose 138, and that the reducing power of dextrose is to that of maltose as 1 to .62; then, calling the weight of dextrose D, of maltose M, and of dextrin d, the reducing sugars R may be represented as $R = D + .62\ M$; the polarization P before treatment with yeast $P = 53\,D + 138\ M + 193d$; and the polarization after fermentation $P' = 193\,D$. From

these equations it may be derived that $d=\frac{P'}{193}$; $D=R-.62\,M$; and $M=\frac{P-P'-53R}{105.14}$.

The sugars formed during the process of malting may be extracted from the malt by cold water and determined in one of the usual ways.

7. The *proteids* in the malt are deduced by determining the nitrogen by the method of Kjeldahl or otherwise, Nesslerizing the distillate (page 376) as the percentage of malt is low. The product of the nitrogen multiplied by the factor 6.25 represents the albuminous matter.

8. *Unmodified starch* is determined by mashing 50 grams of the malt as in (4), then boiling vigorously for an hour. After cooling to 65°, 50 Cc. of a ten per cent cold water extract of malt is added and the whole kept at 65° for an hour. It is then cooled and diluted to 515 Cc., filtered and the specific gravity taken, allowing for the cold water extract added. The specific gravity is calculated to percentage of extractive matter, and the difference between this result and that from (4) is called unmodified starch. The additional features of this process over those of (4) — namely, the boiling and addition of extra diastase — brings the unmodified starch into solution.

9. The residue of '*brewers grains*' from (4) may be washed, dried and weighed.

10. The *color* and *flavor* of the wort are noted. Lovibond* proposes to register the color of malt extracts by preparing a wort by mashing 100 grams of crushed malt in 850 Cc. of water at 74°, and measuring the color in depths of one to nine inches.

Crossman† suggests the following example as a suitable form for reporting the analysis of a malt, mashed under standard conditions: —

Free maltose, fermentable	33.30	
Ready-formed sugars, fermentable	14.08	
Malto-dextrins, unfermentable { maltose, 3.0; dextrin, 1.9 }	4.90	
Free dextrin, unfermentable	13.40	
Albuminoids	2.21	
Ash	1.60	
Acid (as lactic acid)	.51	
Total dry extract	70.00	
Unmodified starch	7.00	
Moisture	1.90	
Grains	21.10	100.00

Diastatic capacity, 30; color of wort, pale; flavor, good.

CELLULOSE.

The celluloses are a group of allied carbohydrates that form the largest constituent of plant tissues. When vegetable fiber is treated successively by alcohol and ether, hot water, a weak solution of an alkali, bromine water, and finally with alcohol and weak lye, cellulose remains in a state of approximate purity, in the form of a colorless or pure white amorphous solid, retaining to some extent the structural form of the plant cell, devoid of taste or odor, having the specific gravity of 1.5, and the empirical formula $C_6H_{10}O_5$.

A peculiar property of cellulose is the presence of a certain definite amount —

* Journ. Socy. Chem. Ind. 1898—207.

† Journ. Amer. Chem. Socy. 16—559.

from six to twelve per cent — of water of condition, the proportion being quite independent of the physical form of the species, and said to depend on the oxy-groups of the molecule, for as these are suppressed by combination with negative radicals to form cellulose-esters, the product has a decreasing capacity for water. Wood-pulp for the manufacture of paper is sold on the basis of a content of ten per cent of moisture.

Cellulose is remarkable for its resistance to nearly all simple solvents. It is soluble however in a few reagents, though less readily after dehydration (as by soaking in alcohol), namely concentrated solution of zinc chloride at 60° to 100°, and a strongly acid solution of this reagent in the cold;* ammoniacal solutions of cupric and cuprous chlorides; sulfuric acid of 1.62 specific gravity. On dilution of the solvent the dissolved cellulose is reprecipitated as a gelatinous hydrate which is soluble in strong nitric acid and alkali solutions and is more readily hydrolyzed by hot dilute acids and alkali solutions. Weak lyes of sodium hydrate (of one or two per cent alkali) are without sensible action even when boiling, but a ten per cent solution hydrates cellulose, and on washing the product with water a hydrate $C_{12}H_{20}O_{10}.H_2O$ is left; a peculiar alkali-cellulose-xanthate is formed by the action of carbon disulfide on this hydrate. A gummy substance isomeric with starch is the result of treatment by diluted sulfuric acid, and with nitric acid of certain high concentrations are produced the well known nitro-celluloses.

Cellulose is less susceptible to oxidation and hydrolysis than the other carbohydrates. It is not fermentable by yeast. On prolonged boiling with a dilute acid it is gradually converted into hydrocellulose. Through the action of moderately dilute nitric acid there are formed oxycellulose (acting as an acid toward coal tar dyes), and oxalic acid. On heating cellulose to 100° with acetic anhydride it is dissolved to a triacetate $C_6H_7(C_2H_3O)_3O_5$, which is precipitated by highly diluting the solution with water.

On account of its negative qualities the separation from other bodies is nearly always made by extracting the latter by suitable solvents and drying and weighing the residue. This residue is called cellulose by some, though more appropriately designated by the more comprehensive term 'crude fibre' since it is always somewhat impure — in point of fact no exact quantitative method of isolating cellulose in a pure state from other vegetable constituents is as yet known; and this is the more to be regretted since its determination is but seldom called for except when so associated.

From sugars and other matter soluble in cold water, cellulose may be separated by simple lixiviation. From starch, boiling the mixture with weak sulfuric acid converts the starch into sugar which may be determined by the polariscope, or otherwise, while the cellulose is left ready to be dried and weighed. If the use of an acid is objectionable, the starch may be converted by malt extract. Honig would heat the mixture with anhydrous glycerol to 210°, cool, and add alcohol and ether which precipitate both the starch and cellulose; then boil with dilute hydrochloric acid to convert the starch to dextrose.

A direct method for the determination of cellulose in presence of vegetable matter is to heat the sample with a ten per cent solution of potassium hydrate to 180° for an hour, then cool the mixture and acidify by dilute sulfuric acid, cellulose hydrate precipitating; on making alkaline by a slight excess of sodium hydrate there is dissolved all but the cellulose. The liquid is filtered, and the residue dried and weighed, then burned and the ash deducted. But the com-

* Chem. News, 1894—1—174.

plete insolubility of cellulose hydrate in dilute alkali solution is very doubtful.

Lange states that cellulose remains undecomposed when heated with a highly concentrated solution of sodium hydrate to a temperature upwards of 200°, while under these conditions other plant constituents become soluble. After lixiviation with water and filtering, the residue is washed, best in a centrifuge* by alcohol and ether, dried and weighed.

For a determination of cellulose in bread, Hoenig† heats two grams with 60 Cc of a solution of potassium hydrate in diluted glycerol. At about 130° a vigorous action begins, increasing up to about 160°. The heat is raised to 180° and the liquid poured into boiling water. After stirring well and allowing to settle, the supernatant liquid is removed by upward filtration through a linen cloth tied over a funnel. The residual fiber is boiled with water and filtered, then washed with weak hydrochloric acid, alcohol, and ether, dried and weighed. It is said that only traces of nitrogenous bodies are left with the cellulose.

An official method for the determination of crude fiber directs to extract the pulverized substance with ether, and boil the residue under a condenser for 30 minutes with water containing 1.25 per cent of sodium hydrate; the residual crude fiber is washed, dried at 110° and weighed, then incinerated and the ash deducted.

Stone proposes the following scheme for vegetable fibers.

1. From 50 to 100 grams of the powdered material is boiled under a reversed condenser for two hours with half a liter of strong alcohol. The *sugars* are dissolved, and after filtering and distilling the alcohol, the residue is dissolved in water and further examined.

2. The matter insoluble in alcohol is next treated with 500 Cc. of cold water to dissolve *soluble starch* and *dextrin*, and filtered through linen. The filtrate is evaporated to a small bulk and an aliquot part inverted and the total carbohydrates determined by Fehlings solution. From another aliquot part the soluble starch may be precipitated by baryta and the dextrin determined in the filtrate by inversion and Fehlings solution.

3. The matter insoluble in cold water is dried and weighed and a portion boiled with water to render starch soluble. The filtered solution is then digested with a fresh infusion of malt at 65° until iodine gives no color; after filtering, the maltose is converted into dextrose by heating with ten per cent hydrochloric acid. The dextrose is then polarized or otherwise determined and the result calculated back to *starch*, an allowance being made for the sugar in the malt extract.

4. The residue left after treatment with malt extract is heated with two per cent hydrochloric acid, converting the *gums* and *pentosans* into reducing sugars to be determined by Fehlings solution and considered as xylose.

5. The residue undecomposed by the dilute hydrochloric acid is heated with sodium hydrate of 1.25 per cent, dissolving certain bodies of an obscure composition.

6. The residue is washed, dried and weighed, then ignited and the residue of *mineral matter* found. The difference between the two weighings is put down as *crude fiber*.

For the analysis of vegetable matter, Parsons ‡ applies various solvents in the following order—

1. Benzene dissolves alkaloids, glucosides, free organic acids, chlorophyll,

* Analyst, 1893—188.
† Prin. & Practice of Brewing.
‡ Pharm. Journ. 10—793.

certain resins, fixed oils, fats and waxes, camphors, and volatile oils, but no mineral matter.

2. Methyl alcohol. Tannin, organic acids, alkaloids, glucosides, certain extractive and coloring matters, resins, sugars, and mineral matters.

3. Cold water. Albuminoids, gums, pectin bodies, salts of organic acids, dextrinoid bodies, and coloring matters.

4. Dilute sulfuric acid. Dextrin and maltose from starch, also albumenoids, and certain organic acids free or combined.

5. Dilute sodium hydrate solution. Albuminous matters, pectous bodies, cutose, humus, and products of decomposition.

6. Bromine water with ammonia. Lignin and coloring matter.

7. The residue is cellulose.

Each of the resulting solutions is further treated to separate the dissolved constituents.

The analysis of woody fiber may be carried out on the following lines. The powdered and dried wood is successively extracted by

1. Water, dissolving various extractive matters.
2. Alcohol and ether, removing various coloring matters.
3. Cold dilute hydrochloric acid — alkaline pectates.
4. Hot dilute hydrochloric acid — pectose.
5. Cold sulfuric acid sp. gr. 1.78 — products from cellulose.
6. Hot dilute sodium hydrate solution — cutose.
7. The residue is lignin ($C_{19}H_{18}O_8$).

Lignin may be directly determined by applying the Zeisel process (page 316). The fiber is boiled with hydriodic acid and the methyl iodide formed is washed in a special apparatus to remove accompanying hydriodic acid; it is then passed into an alcoholic solution of silver nitrate and the silver iodide determined as usual. A current of carbon dioxide is passed continuously through the apparatus.

Lignin has also a reducing action on the compounds of gold, and may be determined by the weight of metallic gold formed on digestion with a solution of auric chloride. The method is applied for the determination of 'mechanical' wood pulp in mixtures.

A number of schemes for the analysis of mixed animal and vegetable fibers have been described, applicable to textile fabrics and waste from their manufacture, and for the determination of make-weights and substitutes in silk.* All aim at a separation by treatment with a succession of solvents. One of these by Remont follows.

1. The disintegrated fibers are boiled in water containing three per cent of hydrochloric acid, to remove coloring matters, size, etc.

2. The residue is immersed in a hot solution of zinc oxychloride which dissolves the silk. The residue is washed, dried and weighed.

3. The residue is boiled with a sodium hydrate solution, sp. gr. 1.02, for 15 minutes, the wool dissolving. The residue of cotton is washed, dried and weighed.

4. True silk is distinguished from 'wild silk' by treatment with hot concentrated hydrochloric acid, the former dissolving in one-half minute, the latter in not less than two minutes. Another reagent is a hot solution of chromic acid which dissolves true silk in one minute.

5. The absolute specific gravity of cotton fibers is 1.50; of wool, 1.30; and of silk, 1.33; weighted silk may reach as high as 2.01.

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* Chem. News, 1893—1—132.

THE OILS AND FATS.

In respect to origin, the oils and fats may be classified as animal, vegetable and mineral. Most of the animal and a few of the vegetable species are solid at ordinary temperatures, while most of the mineral and vegetable are liquid.

The animal and vegetable oils and fats are neutral glycerides of one or more of the fatty acids; since glycerol is a tri-hydric alcohol $(C_3H_5)\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.$, the radical C_3H_5 may be in combination with one, two, or three radicals of a fatty acid; for example, $(C_3H_5)\left\{\begin{matrix}OC_4H_7O\\OC_4H_7O\\OC_4H_7O\end{matrix}\right.$, the tri-glyceride of butyric acid $(C_4H_7O.OH)$, or shortly butyrin. Only the tri-glycerides are found in nature, but the mono- and di-glycerides are produced on heating a fatty acid with glycerol under certain conditions.

A few of the principal glycerides are

1. Tri-olein (commonly called olein) $(C_{18}H_{33}O)_3.O_3.(C_3H_5)$, is a colorless, tasteless and odorless oil, fluid above 5° Cent. and has a specific gravity of .900. It is immiscible with water and diluted alcohol, but is easily soluble in ether and absolute alcohol. Less readily hydrolyzed than palmitin and stearin, it may be roughly separated from these by fractional saponification. Exposed to the air it becomes rancid with the formation of various organic acids and other bodies.

2. Tri-stearin (stearin), $(C_{18}H_{35}O)_3.O_3.(C_3H_5)$, is a white lustrous solid of .920 specific gravity. It may be prepared fairly pure from certain tallows by repeated crystallization from ether. It is but slightly soluble in cold alcohol and ether. Melting point about 70°.

3. Tri-palmitin (palmitin), $(C_{16}H_{31}O)_3.O_3.(C_3H_5)$, is a white mass of pearly scales melting at 62°, but slightly soluble in hot alcohol separating on cooling, and insoluble in water. The body formerly called margarin and considered as a simple glyceride has been shown to be a mixture of palmitin and stearin.

4. Tri-butyrin (butyrin) $(C_4H_7O)_3.O_3.(C_3H_5)$, is a neutral oily mass of peculiar odor and taste, insoluble in water, soluble in alcohol and ether: specific gravity 1.054. Occurs in butter.

The mineral oils of commerce are the distillates of petroleum, said to be mainly aliphatic hydrocarbons of the ethane and ethylene series. The lighter distillates are largely used for heating purposes, the intermediate fractions for illumination, and the heavier for lubrication. Composed essentially of hydrocarbons, they have none of the chemical characteristics of the animal or vegetable oils, and of course cannot be saponified by an alkali. One of the characteristics is the familiar blue fluorescence due to ultra-violet light rays; but the sheen can easily be masked by the incorporation of nitrobenzene or other bodies.

The destructive distillation of rosin yields a series of 'rosin oils' of different specific gravities and boiling points. Unsaponifiable oils are also produced when menhaden or linseed oil is distilled under pressure.

The waxes are a class of solid bodies (a few are liquid) of a peculiar consistency and luster. A wax is chemically an ether, a union of fatty acids with alcohols of the ethane or cetyl series; thus, spermaceti is mainly cetyl palmitate

(cetin) which yields cetylic alcohol (ethal) and palmitic acid on saponification —

$$C_{32}H_{64}O_2 \text{ (cetin)} + H_2O = (C_{16}H_{33})OH\text{(ethal)} + H.C_{16}H_{31}O_2 \text{ (palmitic acid)}.$$

The extraction of a fat or oil from other animal or vegetable matter may be done by expression, or more commonly by treating the finely divided substance with gasoline, ether, or carbon disulfide, rarely alcohol, in a Soxhlet or similar apparatus, these solvents leaving the oil on distillation.

A fat or oil in solution may be determined by simple evaporation of the ether, gasoline or other solvent, or if in an emulsion, by removing the water in some manner and weighing the dried oil, but during the evaporation some varieties will be volatilized to a considerable extent even when the evaporation takes place at ordinary temperatures, and the animal and vegetable oils, especially those of the 'drying' variety, become somewhat oxidized. For the heavier mineral oils however the process is unobjectionable.

The following are the principal physical and chemical tests applied for identification and determination. Sometimes a single test will give the information desired, more often conclusions must be drawn from the results of several. Some of these reactions, almost characteristic for crude oils, are less pronounced in proportion as the oil has been refined, leading to the conclusion that they originate with some impurity eliminated in the refining processes.

1. The *colors* of some crude oils are marked and peculiar, but the mode of extraction, age, etc., may greatly modify them. Refined oils are of every shade to colorless.

Contact with solution of sodium hydrate, sulfuric acid, or nitric acid of certain strengths develops with some oils colors ranging from yellow to brown, and in a few varieties shades of green or purple. Other reagents for this purpose are zinc and tin chlorides, and phosphoric acid. The test is useful as corroborative evidence, but alone is liable to mislead.

The *odor* is often indicative of the origin of an oil or fat; fish oils have a peculiar offensive smell, and rosin, mineral, linseed, and others, can often be recognized in mixtures. But it is not difficult for a manufacturer to disguise or remove an odor unless very pronounced.

The appearance under the *microscope* of certain pure oils is characteristic, but in mixtures the configuration is less distinctive than the proportions of the constituent oils would indicate.

2. The *absorption spectra* of crude vegetable oils, due to chlorophyll, are generally well defined; those of the animal oils are less distinct or altogether wanting.

3. *Specific gravity.* This constant varies greatly for the different varieties, ranging from .875 to .970. It may be observed by means of a delicate hydrometer, the Westphal balance, or the Sprengel tube, attending closely to the temperature and exactness of weighing where accuracy is desired. As with other constants, the results must not be considered as an assurance of the purity or the adulteration of the oil examined, unless corroborated by other tests, for the age of the oil, method of preparation and storing, contact with the air, etc., may alter the accepted constant not a little. Again the change in gravity of a pure oil by the admixture of an adulterant may be corrected by the judicious blending of a third variety, bringing the gravity back to the original figure.

4. *Melting* and *congealing points.* These are often useful as a means of recognition, but no exact constants can be determined for the reason that an oil or fat does not pass sharply from the liquid to the solid state or the reverse, and on

this account there are considerable discrepancies among the figures of different observers, aggravated at times by the fact that portions of a fat coming from different parts of the same animal or vegetable have not a uniform melting point. The methods of determination are described on page 163.

5. The *refractive index** varies from 1.44 to 1.50 at 60° Cent. where water has a refraction of 1.33; it has been shown to bear no relation to the specific gravity, viscosity, or clearness or turbidity of an oil. The refractometer is described on page 167.

6. Relations toward *solvents*. All oils and fats are practically insoluble in water, but, with a few exceptions, freely soluble in ether, carbon disulfide and gasoline; the essential oils dissolve freely in alcohol, but only a few, notably castor oil, of the animal and vegetable oils. In acetic acid of specific gravity 1.056 some dissolve readily, others on heating, and a few are only incompletely dissolved even at the boiling point. As a means of differentiating oils of unequal solubility, first any associated fatty acids are removed, then a certain weight is treated with a limited measured volume of absolute alcohol or glacial acetic acid, filtered, and an aliquot part of the filtrate evaporated to dryness and the residue weighed.†

Acetone dissolves most oils, and in some cases is preferable to any of the usual solvents for certain determinations.

7. *Absorption of oxygen*. Long exposure of a fat or oil to the air results in the formation of greater or less amounts of oxidation products that communicate an unpleasant odor and taste. As the rancidity increases, free fatty acids are liberated, though there does not appear to be any well-defined relation between the degree of rancidity and the acid-value (14) of an oil. By a not well understood series of changes, certain 'drying' or 'semi-drying' oils thicken on exposure to the air and eventually dry to a resinous or leathery skin characteristic of linolein and its homologues. This siccative property, indispensable for a paint-oil, unfits it of course for lubrication or burning.

The proportion of oxygen assimilated by a drying oil in a given time is an indication of its purity, that is, of the absence of a non-drying variety. The rate of absorption is determined by bringing the oil for a specified period into intimate and direct contact with gaseous oxygen, or by mixing with a readily reducible oxide, such as plumbic. Bishop would incorporate with the oil a certain proportion of manganese binoxide and silica and allow the mixture to stand for a certain time. He finds that under these conditions linseed oil absorbs 14 per cent of oxygen in 24 hours.

8. A few of the fixed oils have the property of *reducing salts of silver and gold* to the metals. The test known as Becchi's is applied mainly for the detection of cottonseed oil in olive oil or lard. The method as modified by later investigators, consists in heating the suspected oil in a test-tube with a dilute solution of silver nitrate in alcohol and ether, the formation of a shining deposit of metallic silver on the test-tube indicating the presence of cottonseed oil. Wesson states that even perfectly pure lards may darken under this treatment, due to certain associated bodies, and advises their previous removal by washing the lard with dilute alkali solution and nitric acid. Millian, on the hypothesis that the fatty acids of the oil are most chemically active directly they are separated, would note the action of the silver solution on the freshly prepared mixed fatty acids rather than on the oil itself. Hirchsohn‡ dissolves the suspected oil in chloroform and compounds the

* Journ. Socy. Chem. Ind. 1893—102.
† Chem. News, 1889—1—206.
‡ Chem. Zeit. 12—341.

solution with gold chloride; on heating, cottonseed oil produces a red color.

9. The *elaidin test*. By the action of nitrogen trioxide, olein is converted into an isomer elaidin, and oleic acid into elaidic acid, both of these solid at ordinary temperatures; and according to the proportion of olein in an oil is the solidity of the product. Olive oil, largely olein, gives a characteristic hard mass; neatsfoot oil, one of a buttery consistence; cottonseed oil, a pasty; and linseed oil, a liquid residue. Other oils fall into one of these classes.

The easiest way of applying the test is by dissolving mercury in cold nitric acid; the solution, retaining for a time much of the nitrogen trioxide generated by the reaction, is incorporated with the oil to be tested, and the consistence of the product noted after standing for two hours with frequent agitation.

10. Non-drying oils on treatment with *sulfur chloride* yield products soluble in carbon disulfide, while drying oils change to insoluble solid masses. According to Bruce Warren, the reaction is chiefly a combination of chlorine with hydrogen, the sulfur combining with the dehydrogenized portion of the oil. Five grams of the oil or mixture is weighed in a porcelain dish and mixed with two cubic centimeters of carbon disulfide, then with two cubic centimeters of the reagent (yellow sulfur chloride in carbon disulfide). The mass is evaporated on the water bath to dryness with constant stirring, then dried to constant weight. The residue is finely powdered and extracted by carbon disulfide, the percolate evaporated to dryness and weighed. The process is criticised by Lewkowitsch.*

11. *Exothermic reactions*. When mixed with concentrated sulfuric acid, oils evolve a certain specific amount of heat, the rise in temperature being a function of the chemical action taking place, chiefly saponification. With animal and vegetable oils and fats, for certain specified proportions of oil and acid and strength of the latter, the rise is from 37° to 128° Cent., while the mineral oils show only from 8° to 10°.

In the *Maumene test*, 50 Cc. of the *dry* oil at about 15° Cent. is treated with 10 Cc. of concentrated sulfuric acid; the mixture is constantly stirred with a thermometer and the highest thermal point observed. Since the heat generated varies considerably with the strength of acid, efficiency of the protection against radiation, and other factors, it is best to make a parallel test on pure water and express the result on the oil as the ratio between the two observations.

The combination of bromine with a fat or oil evolves heat approximately commensurate with the ratio of iodine absorbed by the oil (12). Since the rise in temperature is too great for an accurate thermometric measurement, the oil is not compounded directly with bromine, but both are dissolved in chloroform or other solvent before mixing.

12. *Halogen absorption*. The oils and fatty acids of the oleic and acrylic groups form additive compounds with bromine and iodine in contradistinction to those of the (saturated) stearic and acetic series. Huebl,† the originator, recommends dissolving a fraction of a gram of the oil in chloroform and mixing with an excess of a standard solution of iodine in alcohol containing mercuric chloride (which acts to hasten the assimilation of the iodine by the oil). After standing for two to four hours in a dark place at the ordinary temperature the mixture is diluted with a weak solution of potassium iodide (water alone might precipitate mercuric iodide), and the unabsorbed iodine

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* Benedikt-Lewkowitsch, Oils, Fats and Waxes, 228; Chem. News. 1888—1—113 and 1890—2—5 etc.

† Chem. Zeit. 13—1375.

titrated by sodium thiosulfate that has been standardized against iodine. A blank determination is carried along with the test.

Several modifications of the reagent and the manner of applying it have been described. Wijs commends a solution of iodine chloride in glacial acetic acid as preferable to the original Huebl in being more stable and requiring a shorter time for the reaction to be completed.

The method applied to a mixture of two oils whose absorbent capacities differ considerably, is capable of giving an approximate determination of their proportions, but usually is only qualitatively applied as a test of purity. For example, genuine olive oil absorbs from 81 to 85 per cent of its weight of iodine, while cottonseed, rape and sesamé oils, its most common adulterants, absorb from 97 to 108 per cent when unrefined, somewhat less when highly refined. The ratio of iodine absorbed is higher for fats and oils than for their respective fatty acids.

The absorption of bromine is determined by Hehner* by dissolving a gram or more of the oil in chloroform in a tared flask; bromine is added drop by drop to slight excess, then heated until the excess of bromine and the chloroform are driven off. The gain in weight of the oil is claimed to represent the bromine absorbed.

McIlhiney† points out that bromine may be fixed in two ways, (1) by replacing hydrogen, one atom of bromine displacing one atom of hydrogen which combines with another atom of bromine forming a molecule of hydrobromic acid; and (2) by direct addition to the unsaturated groups of the oil, not forming hydrobromic acid. The parts of bromine absorbed by 100 parts of oil in (1) he calls the "bromine substitution figure".

The method recommended is to dissolve the oil or resin in carbon tetrachloride and add an excess of third-normal bromine in the same solvent. The bottle is stoppered and kept in the dark for eighteen hours, then water added to dissolve the hydrobromic acid formed, with precautions to prevent its escape in gaseous form. Excess of potassium iodide is added and the iodine (liberated by the excess of bromine) titrated by thiosulfate and starch; the result is calculated to bromine, and the difference between this and the weight of bromine originally added is the total bromine absorbed.

The liquid is filtered through linen, and the aqueous solution, containing free hydrobromic acid, titrated to neutrality by standard alkali and methyl orange, giving the bromine substitution figure. The total bromine absorbed minus *twice* the bromine substitution figure equals the "bromine addition figure." For example, for rosin oil the total bromine figure (percentage) is 116.2; the bromine substitution figure 58.1, and the addition figure zero; while with linseed oil the corresponding numbers are 102.9, zero, and 102.9.

13. The *acetyl-value.*‡ Certain fatty acids that contain an alcoholic hydroxyl group react to form an acetyl-fatty-acid on heating with acetic anhydride; thus the ricinic acid from castor oil,

(1). $C_{18}H_{34}O_3$ (ricinic acid) + $(C_2H_3O)_2O$ (acetic anhydride) =
$C_{18}H_{33}O_3.C_2H_3O$ (acetyl-ricinic acid) + $HC_2H_3O_2$ (acetic acid).

On treatment of the acetyl-ricinic acid with standard potassium hydrate an atom of potassium replaces one of hydrogen with the formation of water—

(2). $C_{18}H_{33}O_3.C_2H_3O$ (acetyl-ricinic acid) + KOH = $C_{18}H_{33}KO_3.C_2H_3O$ (potassium acetyl-ricinate) + HOH.

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* Analyst, 1895—50.

† Journ. Amer. Chem. Socy. 1894—275 and 1899—1064.

‡ Analyst, 1899—319.

But on heating the potassium acetyl-ricinate with an excess of potassium hydrate in alcohol, hydrolysis takes place with the formation of potassium ricinate and acetate —

(3). $C_{18}H_{32}KO_3.C_2H_3O$ (potassium acetyl-ricinate) $+ KOH =$
$KC_{18}H_{33}O_3$ (potassium ricinate) $+ KC_2H_3O_2$ (potassium acetate).

The weight of KOH required in equation (3) for one gram of acetyl-ricinic acid is called the "acetyl value." Oleic, stearic, palmitic, etc., acids containing no hydroxyl groups give (theoretically) no acetyl value as the reaction of equation (3) does not take place.

The process is as follows: A large quantity of the oil is hydrolyzed and the fatty acids washed and dried and boiled with acetic anhydride. After dilution with water the floating layer of acetylated acids is removed and thoroughly washed with hot water. A weighed portion of the dried product is dissolved in neutral alcohol and titrated by standard potassium hydrate and phenolphthalein. As soon as the red color appears a measured excess of alcoholic standard potash is run in, and after boiling, the excess titrated by standard acid, and from the volume of acid is calculated the weight of potash required for equation (3); or the liquid may be acidified by sulfuric acid, and the freed acetic acid (from the potassium acetate) distilled and determined in the distillate.

14. The *acid value.* Nearly all commercial samples of the animal and vegetable oils contain from a fraction of one per cent up to several per cents of free fatty or organic acids, either as normal constituents or resulting from decomposition by age or exposure to the air. For illumination and lubrication a neutral oil is always preferred, as acids tend to char amp wicks and corrode metallic bearings. The determination is made by heating the oil with neutral alcohol in which the fatty acids are easily soluble, and titrating by weak standard alkali and an indicator like turmeric or litmus. The mixture must be well stirred before titration to emulsify the oil and bring the alcohol and acids into contact.

15. The *ether value.* The animal and vegetable oils are made up of neutral glycerides of various fatty acids, and when distilled in superheated steam are hydrolyzed into free fatty acids and glycerol; thus

$$C_3H_5O_3.R_3 \text{ (neutral fat)} + 3H_2O = R_3.(OH)_3 + C_3H_5O_3 \text{ (glycerol)},$$

where R is the radical of any fatty acid. Similarly when saponified by a caustic alkali,

$$C_3H_5O_3.R_3 + 3NaOH = R_3.(ONa)_3 + C_3H_5O_3.$$

Other reagents for saponification are concentrated sulfuric acid, sodium alcoholate, bromine, etc., sometimes used for special material.

The ether value is the number of milligrams of potassium hydroxide (KOH) required to saponify one gram of a neutral oil or fat, and is determined by emulsifying the oil with alcohol, neutralizing any free fatty acids by potassium hydrate, heating the liquid with a known volume of standard alcoholic solution of potassium hydrate, and determining the excess of alkali by titrating back by standard acid.

With the exception of butyric and a few associates found in butter and cocoanut oil, the fatty acids are not volatilized in a current of steam at atmospheric pressure. The '*Reichert test,*' an important feature in butter analysis, withdraws and determines the volatile members from the mixed fatty acids; the process is essentially a distillation of the mixed acids with water and titration of the acids in the distillate by standard alkali. Scala supports the plan of accepting the proportion of volatile fatty acids in fats other than butter as a criterion of the degree of rancidity.

16. *Saponification.* In the laboratory, saponification is easiest accomplished by heating the oil or fat with a solution of potassium or sodium hydrate. Since the rapidity of the reaction is the greater the more intimate the contact between the oil and alkali, an alcoholic solution of the latter is generally preferred to an aqueous one, though concentrated lyes of caustic soda or a mixture of caustic soda and potash at boiling heat act energetically. An excellent means of hastening the decomposition of the less easily saponified bodies, such as the waxes, was devised by Henriques,* namely, by dissolving the oil or wax in ether or gasoline before the addition of the alcoholic alkali solution; saponification is complete at ordinary temperatures within a few hours. By conducting the operation without application of heat, no ethers of the volatile fatty acids are formed, as occurs to a slight extent under the higher temperatures of the ordinary process.

As saponification proceeds, the fatty acids combine at once with the alkali to form soaps; thus the transformation of lard by potassium hydrate —

$$C_3H_5(C_{18}H_{35}O_2)_3 + 3KOH = C_3H_5(OH)_3 + 3K(C_{18}H_{35}O_2)$$
Stearin — Glycerol — Potassium stearate.

$$C_3H_5(C_{18}H_{33}O_2)_3 + 3KOH = C_3H_5(OH)_3 + 3K(C_{18}H_{33}O_2)$$
Olein — Potassium oleate.

$$C_3H_5(C_{16}H_{31}O_2)_3 + 3KOH = C_3H_5(OH)_3 + 3K(C_{16}H_{31}O_2)$$
Palmatin — Potassium palmitate.

Saponification is employed for the following purposes:

(1) To obtain the fatty acids for a physical or chemical examination. On acidifying the hot solution of the soaps obtained by the action of an alkali on an oil, the fatty acids are liberated and float as an oily layer on the surface. Thus with lard soap —

$$3K(C_{18}H_{35}O_2) + 3HCl = 3KCl + 3HC_{18}H_{35}O_2 \text{ (stearic acid).}$$
$$3K(C_{18}H_{33}O_2) + 3HCl = 3KCl + 3HC_{18}H_{33}O_2 \text{ (oleic acid).}$$
$$3K(C_{16}H_{31}O_2) + 3HCl = 3KCl + 3HC_{16}H_{31}O_2 \text{ (palmitic acid).}$$

and the mixture may be separated from the solution of potassium chloride and glycerol by decantation or filtration.

The alcoholic liquid is evaporated to dryness on the water bath, taken up with hot water, acidified, and filtered through a close paper, the aqueous liquid passing through; or the liquid may be cooled and the solidified cake of fatty acids separated by pouring out the water solution. The reason for changing the alcoholic solution to an aqueous one before acidulation is that fatty acids are somewhat soluble in alcohol. The fatty acids are washed with water, then dried at a temperature not much exceeding 100°.

Lactones, like the glycerides, yield soaps on saponification; on acidification the lactones are reprecipitated.

(2) To determine the ether value. The ether value is the number of milligrams of potassium hydrate required to saponify one gram of a neutral oil. The process requires an accurately standardized alcoholic solution of potassium hydrate of which a measured volume, largely in excess of that needed for saponification, is heated with a weighed amount of the previously neutralized oil. When the oil has been fully decomposed, as evidenced by the absence of oily globules, the excess of alkali is titrated by standard hydrochloric acid, or by standard sulfuric acid after dilution with water to prevent the separation of potassium sulfate during the titration. With dark colored oils, especially when an old and brown solution of alkali is used, the change of the indicator is obscured and it has been recommended to distill the solution with an excess of

* Analyst, 1896—67 and 192.

ammonium chloride and titrate the free ammonia in the distillate corresponding to the excess of potassium hydrate — $KOH + NH_4Cl = KCl + NH_4OH$.

The *saponification value* is simply a convenient technical expression for the sum of the acid and ether values; and may be stated either as *Koettstorfer's number*, the number of milligrams of potassium hydrate saponifying one gram of an unneutralized oil or fat, or as the *saponification equivalent*, the number of grams of an oil saponified by one liter of strictly normal potassium or sodium hydrate. The former is the quotient of 56112 (that is, the molecular weight of potassium hydrate times 1000) divided by the latter. Obviously, with a neutral oil the Koettstorfer number is also the ether value; and on the other hand, the Koettstorfer number of a pure free fatty acid equals the acid value, and the ether value is zero.

(3) To identify an animal or vegetable oil. As will be seen from the equations on page 458, three molecules of KOH (168.354) decompose respectively one molecule (890.88) of stearin, one molecule (884.82) of olein, or one molecule (806.79) of palmitin. For a mixture of these fats in a fairly constant ratio, such as lard, the weight of alkali saponifying one gram is a constant differing more or less from those of other fats or oils. A greater variation is where butyrin, laurin, and similar glycerides are constituents.

The physical and chemical constants of a few of the common oils are tabulated below. They are averages of results, differing considerably in some cases, obtained by several observers.

Species	Specific gravity.	Congeals ° Cent.	Maumené test.	Koetts. number.	Iodine number.	Acetyl value.	Refractive index (Jean's).
Olive	.9165	2	41	191	82	4.7	1.5
Sesamé	.9210	— 5	65	190	107	11.5	18.
Cottonseed	.9220	— 2	75	193	109	16.6	18.
Linseed	.9350	— 27.5	105	193	172	8.5	50.
Castor	.9655	— 17	46	179	83	153.4	40.
Almond	.9180	— 10	52	191	97	5.8	6.5
Rape	.9140	— 3	60	175	101	6.3	17.5
Lard oil	.9145	7	45	194	79	3.1	5.5

Descriptions of the many special tests for the detection and determination of adulterants and substitutes will be found in the treatises on oils and oil analysis.

The analysis of a mixture of oils is often a difficult problem and the outcome not infrequently open to doubt. The separation of a saponifiable from an unsaponifiable oil offers no particular difficulties, but mixtures of either class seldom admit of direct separation. Attributive methods can often be applied to two or possibly three mixed oils, the data derived from their specific gravities, iodine absorption, sulfur chloride reaction, etc. And in a binary mixture, if the species of one member can be learned, that of the other may be opined by a comparison of a constant of the former and that of the mixture (page 156).

A scheme for the general course of analysis is outlined below, but it is seldom that any detailed directions can be followed without considerable modification.

1. The color, odor, taste, and general appearance will often be a clue to one or more of the constituents. A specific gravity below .900 indicates mineral or light rosin oils entirely or chiefly, and above .975, heavy rosin or tar oils. The great majority of pure oils and mixtures have a gravity between .900 and .975.

2. The sample is treated with carbon disulfide. In this menstruum all oils are soluble, but not the soaps. If a residue remains, the solution is filtered,

washed by carbon disulfide, the residue weighed and decomposed by a dilute mineral acid, and the resulting fatty acid and salt of the base examined qualitatively.

The carbon disulfide is evaporated from the filtrate, and the remaining oils treated with warm alcohol; free fatty acids dissolve, together with castor, croton, olive-kernel and rosin oils, while other oils remain. If a clear solution results, only the above mentioned may be present; if not, the liquid is filtered and the alcohol evaporated from the filtrate to see if any oil has been taken up by it.

3. The sample is moderately heated in a copper retort connected to an efficient condenser; the distillate will consist of the more volatile hydrocarbons, rosin oils, turpentine, etc., which might escape detection in (4). Water, an occasional constituent, is found at the bottom of the receiver, and may be tapped off in a separatory funnel and measured or weighed.* A more accurate method for determining water is to stir into the original oil, diluted if necessary with dried gasoline, a weighed quantity of recently ignited calcium sulfate. The liquid is filtered, washed with gasoline, and the increase in weight of the calcium sulfate noted.

4. For the detection of animal and vegetable oils and their separation from mineral or rosin oils, the sample is boiled with an alcoholic solution of potash under a reflux condenser. The alcohol is evaporated off at a low heat, the residue taken up with hot water, and some sodium bicarbonate stirred in. Two cases may result.

A. The solution is clear and free from oily drops, indicating that the sample is entirely animal or vegetable, possibly containing a rosin or wax or bearing a small proportion of mineral or rosin oil which remains in solution.

B. On the surface floats oily matter. The sample is then either entirely mineral or rosin oil or a mixture with a saponifiable oil. Of the two layers the upper is the mineral or rosin oil, the lower a solution of potash soaps of the fatty acids with glycerol and the excess of alkali as carbonate. The object of obtaining an aqueous solution is to avoid the loss of small quantities of unsaponifiable oils through their solubility in alcohol.

In either case the liquid is transferred to a separatory funnel and the unsaponifiable oils extracted by ether or gasoline; this plan is preferable to simply tapping out the aqueous solution. The extraction is continued until a few drops of the ether leave no residue on evaporation. The separation is not quite complete, however, traces of the unsaponifiable matter remaining in the alkaline solution, while a little soap enters the gasoline. The ether solution is washed with water to remove traces of dissolved soap, and the water washed in turn by ether to recover any unsaponifiable matter taken up by it

The ethereal solution is evaporated to dryness and the residue weighed. It may consist of mineral or rosin oils or a mixture of the two, and may be examined as on page 478. Possibly also there are higher alcohols of the ethane series (rutic, cetylic, etc.), that may be determined from their acetyl value or the volume of hydrogen evolved on heating with potash-lime, page 399. If the residue appears to be homogeneous (consist of but one body) an ultimate analysis or appropriate physical tests may show its nature, and if composed of two or more analogous bodies they may be separated by fractional solution, fractional crystallization from ether, or like means.

The unsaponifiable matter may be a mixture of mineral and rosin oils. A rough separation of the two can be accomplished by treating the mixture

* Hopkins' Oil-chemists' Handbook, 30.

with alcohol, rosin oils being freely soluble therein, while mineral oils are but sparingly soluble. To recover as far as possible what mineral oil has gone into solution, the alcoholic filtrate is evaporated to dryness and the residue extracted by alcohol, when much of that originally dissolved will be left.

(The process may be made somewhat more exact by repeating the above extraction with a smaller volume of alcohol than the first, measuring the volumes of alcohol used and weighing the respective residues. Obviously the difference between the volumes of alcohol is the volume that would dissolve a weight of mineral oil equal to the difference in the weights of the residues; and knowing the rate of solubility of the mineral oil in alcohol, the amount in the last residue may be easily calculated, and from this the weight of rosin oil by difference. No account is here taken of the solvent effect of the rosin oil in the alcohol.)

The aqueous solution, plus the traces of soap recovered from the gasoline, is acidified by hydrochloric acid and heated until a clear layer of the melted fatty acids floats on the solution of potassium chloride and glycerol. After filtration, the fatty acids may be dried and weighed, then washed with acetone to dissolve out small amounts of unsaponifiable matter retained in the aqueous solution. The combining power or mean molecular weight of the mixed acids can be determined by dissolving in an excess of standard potassium hydrate solution, and titrating back the excess by standard acid. The majority of the fixed oils yield 95 to 96 per cent of fatty acids and about 10 per cent of glycerol (the extra 5 per cent coming from the assimilation of water).

A short approximate method for the determination of the animal or vegetable oil in admixture with mineral or rosin oil (as are many of the lubricating and burning oils of commerce) consists in finding the saponification value of the sample in the usual way. If the species of the saponifiable oil is known the proportion in the mixture will follow from the ratio of the saponification value of the sample to the value established for the pure oil, or if the species is unknown, the mean of the values of the oils in common use for the purpose intended for the sample. A closer result may be had by syphoning off a part of the floating mineral oil, determining its specific gravity, and modifying the calculation accordingly.

Technical analysis. The oils and fats are used mainly for illumination, lubrication, food, the manufacture of soaps and candles and paints and varnishes, and the preparation of cloths and skins. The technical analyst has both to determine the intrinsic quality for a given purpose of the material he is to examine, and, as far as he is able, to learn if adulteration or substitution has been practiced. A comprehensive scheme for the analysis of mixed oils cannot be formulated, much depending on the judgment and experience of the analyst, who must keep clearly in mind the objects for which the analysis is made.

Illuminating oils. At the present time these are largely the intermediate distillates of petroleum, the ordinary kerosene of 45° Baume, and the 'mineral seal oil' of 39° Baume. Their cheapness precludes any adulteration, and if of the proper gravity and clearness, the analyst has but to examine for their safety for burning in ordinary lamps, and occasionally determine their congealing temperatures.

The flash and burning temperatures. The 'flash-point'* is the temperature

* Chem. News, 1893—1—291.

whereat a liquid gives off vapor so freely that the mixture of vapor and air above the surface will burn for an instant when brought in contact with a flame. If the liquid is a mixture of two or more of different boiling points, the flash-point is usually higher than that of the most volatile constituent. The 'burning-point' is the temperature at which the liquid itself will take fire and burn continuously when touched with a flame (very small, to prevent local heating). Certain minimum flash and burning points indicate the safety of an oil for illuminating or heating purposes. For kerosene the legal minimum in many States is a flash-point of 110° Fahr. (closed cup), and a burning-point of 150°; for the next heavier distillate of petroleum, known variously as 'mineral seal', 'Iowa oil', etc., they are respectively 235° and 300° Fahr.

In all the various forms of apparatus for determining these points, the oil is contained in a metal cup arranged to be heated slowly and uniformly to the required temperatures. The instrument authorized by the New York State Board of Health is shown in section in Fig. 179. For testing kerosene the cup A is filled nearly up to the flange B, and a glass plate C holding a cork and thermometer D is laid on the upper flange E. The outer cup F acts as a water-bath and is nearly filled with cold water and heated by a small flame of a Bunsen burner beneath, so adjusted that the temperature of the oil shall not rise at a greater rate than two degrees Fahr. per minute. At each accession of two degrees, a minute flame is passed through a small hole in the glass plate, and at the moment when a flash of light is observed in the empty space, the temperature of the oil is read, the flash-point.

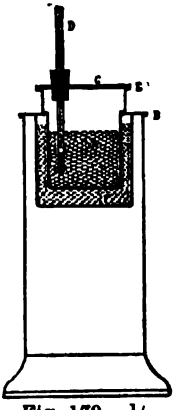

Fig. 179 $^1/_7$

Where the flash or burning point is above 100°, the outer cup is filled with oil or paraffin. For very high temperatures a sand bath is used.

Apparatus of this description wherein the vapor is largely prevented from diffusing into the air are known as "closed-cup," as distinguished from those without the glass plate, called "open-cup." The former afford readings considerably lower than the latter and are generally regarded as more reliable.

To determine the burning-point, the glass cover is removed and the thermometer bulb hung in the oil. The heat is slowly increased until the oil catches fire and burns quietly when a minute flame is passed rapidly over the surface about an inch above it.

Distillation. The lighter mineral and rosin oils distill at moderate temperatures and can be separated in this way from less volatile bodies. Fractional distillation effects the separation of the various homologues of crude and partially refined petroleum or rosin oils, previously removing any water or sedimentary matter by allowing the oil to stand in a tall jar for a day or longer. The distillation is conducted in a porcelain or metal apparatus in the usual manner. The receiver is changed at periods indicated by the temperature of the vapor in the still; if a technical analysis, at certain arbitrary points conforming to the commercial classification of the products. For example, a petroleum from Ohio gave on distillation —

	Specific gravity.	Yield per cent.
Gasoline,	.630	2.
Naptha,	.700	15.
Kerosene,	.800	55.
Paraffin oil,	.875	20.
Coke left in retort,	....	8.

The further examination of a mineral oil may include the following.

1. The colors of kerosene are expressed in trade parlance as water-white, superfine white, prime white, standard white, and good merchantable. For comparison of a sample with the standards a Wilson's, Stammer's, or Redwood's colorimeter may be used.

2. Calcium and magnesium salts in an oil diminish the illuminating power. A volume of 100 to 200 cubic centimeters is evaporated to dryness, the residue ignited, dissolved in hydrochloric acid and the bases determined by the usual methods.

3. Earthy and alkali soaps. The metaphosphates of these bases are insoluble in absolute alcohol or a mixure of absolute alcohol and gasoline. The soaps are looked for by dissolving a few drops of the suspected oil in a little gasoline and compounding with a saturated solution of metaphosphoric acid in absolute alcohol. The formation of a flocculent precipitate on standing for a time shows the presence of a soap. The base may be identified by the usual qualitative tests for the earthy and alkali phosphates.

4. Matter volatile below 65° Cent. About .2 gram of the oil is imbibed in a disk of filter paper, this heated for eight hours on the water bath at 60° to 65°. The loss in weight is that of volatile matter and water if present.

5. Rosin as an adulterant can be determined by heating the oil with nitric acid and extracting the mineral oil by ether. The products of the action of the acid on the rosin remain insoluble. The mineral oil loses about ten per cent in weight.

6. Sulfur is usually determined by burning the oil in an apparatus arranged to oxidize and retain the combustion products of the sulfur compounds. Sulfuric acid (from refining processes) can be washed from the oil by water; it is all retained, as well as some sulfur compounds of the oil, when the latter is distilled with sodium bicarbonate.

Lubricating oils. The value of an oil as a lubricant depends on a combination of several qualities of which the chief is that the oil shall possess sufficient adhesiveness to prevent the contact of the metallic surfaces, and that its cohesion or viscosity shall approach the limit where internal friction becomes a detriment. For example, a mineral oil is suited to a slowly moving pinion bearing a moderate load; under a heavy load the adhesion of a mineral oil would be overcome, unlike some vegetable oils, such as castor, whose adhesion persists even under heavy pressure.

The viscosity of an oil may be determined in several ways, the most common that of observing the period of time consumed for a given volume to flow through an orifice of standard area as compared with that for water or a certain oil taken as a standard. The viscosities of the oils differ greatly, that of raw linseed, for example, being only one-half that of olive. The temperature has a marked influence on the rate of flow; thus, a specimen of mineral oil requiring 1030 minutes to pass a certain orifice at 50° Fahr. took only 680 minutes when at 60°, and 40 minutes at 212°.

A simple 'viscosimeter' is a pipette holding 100 Cc. between two marks, one above, the other below the bulb. The orifice at the bottom is of such an area that 100 Cc. of water at 100° Fahr. will run out in 34 seconds. The oil to be examined is heated to 100°, or higher if very viscid, and the pipette filled by suction; the number of seconds required for the outflow of the volume of oil held between the marks is called the 'viscosity number' of the oil.

Obviously, the temperature of the oil is continually falling during the outflow, and the hydrostatic pressure diminishing. To eliminate these objection-

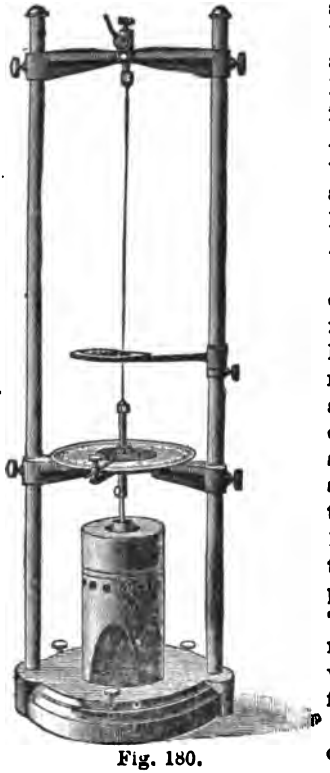

Fig. 180.

able features, a number of instruments have been invented wherein the pipette or its equivalent is surrounded by a bath of some liquid heated to a given constant temperature and kept in motion by a stirrer to avoid local overheating. And instead of measuring the outflow by the volume discharged, the oil-reservoir is kept full and the oil drawn into a measuring cylinder. For a detailed description refer to the Journ. Anal. and Applied Chem. V—314 et seq.*

Other apparatus are based on a different principle, namely the resistance opposed to the movement of a solid body in the oil; though it has been questioned whether this retardation really measures viscosity. Cockrell's device is a small paddle revolved in the oil by means of clockwork, the coefficient of retardation in speed as compared to that in water being considered a measure of the viscosity. Doolittle's torsion viscosimeter † is a metal cylinder, Fig. 180, 2 inches high by 1.5 in diameter, hung vertically in the oil by a long steel wire bearing a pointer traversing a horizontal graduated circle. The amplitude of the arc described by alternate rotations of the cylinder in air is diminished when the cylinder is held in a liquid, and is referred to pure water as a standard.

Kunkler contends that the viscosimeter gives data of practical value with mineral oils only, since the adhesion of the other oils to metal bearings does not increase with the viscidity.

In the technical examination of lubricating oils, the so-called "cold-test" is observed by half-filling a long narrow bottle with the oil and immersing it in a freezing mixture until the oil is solidified. The bottle is removed to a warm place and the oil constantly stirred with a thermometer until it just begins to flow, or, as others direct, until it will just flow from one end of the bottle to the other.

The flash and burning temperatures are useful tests of a lubricant and may detect the presence of a light mineral or rosin oil in a supposedly simple animal or vegetable one.

Lard oil has a large consumption as an illuminant either alone or in admixture with a mineral oil, and for this purpose should not contain more than one or two per cent of free fatty acids, and be free from the cheaper, though less suitable, cottonseed and tallow oils.

In paints and varnishes linseed oil is an important constituent. The drying quality is greatly increased by boiling for a certain time, and addition of 'dryers' (litharge, etc.). The examination for adulterants should be mainly in the direction of the cheaper corn, cottonseed or rosin oils, not overlooking the possible incorporation of mineral oil. A test of the rapidity of drying, sometimes of importance, can be made by spreading a thin film on a sheet of

* Stevens Inst. of Tech. Indicator, 1899—251.

† Journ. Amer. Chem. Socy. 1893—173; and Chem. News, 1893—1—168 and 296.

glass and noting the number of hours required for the film to set and to harden.

Paints are generally put on the market in paste form, that is ground up with ten to twenty per cent of boiled linseed oil, or 'ready mixed' containing a much larger proportion of oil, and usually certain dryers. To separate the oil from the pigment, the paste may be boiled with ether or other organic solvent and filtered through a very closely-woven paper, and the pigment washed with ether. The oil is obtained for examination by evaporating off the ether at a low heat; certain gums and resins may also be contained if the paint was a 'gloss' or 'varnish' paint.

The common organic solvents, however, do not dissolve the oil of a paint to a perfectly homogeneous liquid, the solution being somewhat gelatinous. Hanney* finds that methylated ether (ordinary ether plus ten per cent of methylic ether) when used in the proportion of 100 Cc. to one gram of paste yields a perfect solution of the oil and allows decantation from a heavy pigment. When a sample of paint is already mixed with the proper proportion of oil and dryers for immediate application, simply diluting it with gasoline and whirling in the centrifuge will allow the liquid to be decanted off clear.

Repeated evaporations with concentrated nitric acid will sometimes destroy the oil completely and leave the pigment, this usually somewhat altered from the original composition, except in the case of barite, silica, etc.

Varnishes, from the nature of their ingredients and some obscure changes in chemical composition during or after manufacture, present a difficult problem to the analyst — in fact, a practical test of the flowing qualities, covering power, gloss, and resistance of the coat to abrasion and the weather is likely to be of more practical value than an analysis.

TURPENTINE.

Turpentine is an essential oil distilled by steam from the resinous exudation of the yellow or Georgia pine tree, and is largely used in the manufacture of paints and varnishes. It is a nearly colorless, limpid, inflammable liquid, composed of several polymers (terpenes) of the formula $C_{10}H_{16}$. Exposed to light and air certain changes take place, culminating in the formation of a resinous crystalline body of the formula $C_{10}H_{18}O_2$.

Turpentine is sometimes adulterated with a small proportion of petroleum spirit, rosin oil, paraffin oil, or shale spirit. Their detection and determination is difficult, especially when they are in but small proportions.

1. The specific gravity of commercial turpentine ranges from .860 to .875, the average about .867. Should the gravity of a sample be below .860 there is indicated rosin oil (.856 to .860), or petroleum distillates or shale naptha (.700 to .830); if above .875, paraffin oil (.890), or a fat oil (.912 to 937).

2. The molecular weight is about 138.6 to 147.7. The vapor density is from 4.80 to 5.11. Light petroleum distillates give lower values than these. It has been recommended to fractionally distill the sample and determine these constants in the first fraction.

3. The flash-point is quite constant at 32° to 33°; the boiling point at 155° to 158°. If below these temperatures there is indicated an admixture of light petroleum oils; if above them, paraffin or fat oils. However, ordinary petroleum distillates used for burning purposes have approximately the same flash or boiling point as turpentine.

* Chem. News, 1893—1—268 and 301.

4. On evaporation in a current of steam, fresh turpentine should not leave over .2 to .5 per cent of residue, old samples from .5 to 2 per cent. The resinous matter left on evaporating old turpentine is dissolved by nitric acid, a distinction from heavy petroleum or fat oils.

Hinsdale * directs to put ten drops of a suspected sample on a watch glass, weigh, and float the glass on water kept at 170° Fahr. If pure it will have evaporated in about seven minutes; any considerable residue is considered proof of adulteration with petroleum. A parallel test is made with pure turpentine, and when this has evaporated the glass containing the sample is weighed. Five per cent of petroleum is said to be detectible by this process.

5. Distillation of turpentine begins at about 156°; about 85 per cent passes over below 163°, and nearly all below 185° to 190°. The usual adulterants begin to distill below 160°, and the final temperature is above 190°, fat oils remaining. It is best to attach a dephlagmator to the distilling flask. Phillips † in separating turpentine from ready-mixed paints, distills the paint at 225° in a current of coal-gas to prevent oxidation of the residue.

6. Polymerization. By cautious treatment with concentrated sulfuric acid, moderating the action by cooling the flask, turpentine is polymerized into bodies soluble in concentrated sulfuric acid. Armstrong proposes to treat 500 Cc. of the sample with 150 Cc. of sulfuric acid (two volumes of acid to one of water), pour the mixture into a separatory funnel, and tap off the solution of the polymers. The residual liquid is distilled in steam and the distillate treated with stronger acid, when the residue should not exceed 25 Cc. If of greater volume it is mixed with several volumes of very concentrated acid and heated to 122° Fahr., when the residue should not exceed 2.5 Cc. Petroleum products and paraffin oil are practically unaffected by sulfuric acid, but rosin spirit is acted on to a considerable extent.

A simple test is made by mixing 30 Cc. of concentrated sulfuric acid with six Cc. of the turpentine in a graduated tube, uniting the two slowly and cooling the tube in water to prevent any great rise in temperature. After thorough agitation the mixture is allowed to stand for a few hours, when the floating layer should not exceed .3 Cc. in volume.

A process similar to that of Armstrong is described by Burton. On mixing turpentine with fuming nitric acid there are formed oxidation products soluble in water. After washing out soluble matter with hot water the residue should not exceed two per cent by volume of the original.

7. Turpentine is dextro-rotatory to polarized light, different samples showing 8° to 16° for American turpentine.‡ Armstrong considers American products to contain two terpenes, one dextro- and one laevo-rotatory.

BEESWAX.

The most familiar of the wax family is the well-known beeswax, a mixture of myricyl palmitate, cerotic acid, certain hydrocarbons, and small quantities of allied acids and alcohols. The natural color is pale yellow, changed to pure white by bleaching in sunlight or by chemical agents. The most common of the adulterants are yellow paraffin or ceresin for beeswax, and white paraffin or ceresin for white wax.

The specific gravity of pure wax ranges from .956 to .964, usually lying

* Chem. News, 1891—1—161.
† *Idem*, 1891—1—275.
‡ Journ. Anal. Appl. Chem. 1892—1 and 1893—99.

between .958 and .961. The gravity of ceresin is from .915 to .925, while that of paraffin is from .865 to .908. A gravity of above .964 points to adulteration with stearic acid, rosin, etc., and below .956 to paraffin, ceresin, or tallow.

The specific gravity is conveniently observed according to Liverage by cutting a small cube from the interior of a cake and weighing by the Westphal balance, supporting the cube by inserting the pointed end of the plummet. Allen prefers to determine the gravity of the melted wax at 100°, it ranging at this temperature from .818 to .827.

The microscopic appearance of pure wax crystallized from chloroform is characteristically crystalline; paraffin in amounts of over 20 per cent discomposing the crystals.

The melting point is from 61° to 64°, the solidifying point about the same. Paraffin melts at from 35° to 58°; ceresin from 68° to 89°; and spermaceti at about 45°.

The refractive index as registered by the Zeiss refractometer varies from 42.6° to 45.4°; paraffin, 22.5°; ceresin, 41.0°; and tallow, 48.5°. All these figures were calculated to 40° Cent. from the readings at 66° to 72°.

The examination of a commercial wax may be conducted about as follows.

Water is determined by melting the wax and allowing it to cool slowly to solidification, when most of the water will collect at the bottom of the dish and may be poured out and weighed. The solidified wax is then dried at 100° to constant weight. Mineral make-weights or colors, such as ochre, barite, clay or gypsum, separate from the melted wax with the water and may be recognized by examination with a lens or by qualitative tests.

The *acid number*. Five grams of the wax is melted with 20 Cc. of neutral strong alcohol, and the mixture titrated by half-normal potassium hydrate and phenol-phthalein. The number of milligrams of potassium hydrate required to saturate the cerotic acid of one gram of wax is called its acid number; it is about 19 to 21 — high as compared with those of the oils and fats.

The *ether number*. The neutralized solution of the wax obtained as above is heated with a measured volume of standard potassium hydrate in alcohol to saponify the myricyl palmitate; the ether number (milligrams of potassium hydrate per gram of wax) is found by a reverse titration by standard acid. It ranges from 73 to 76, and the saponification number (acid number plus ether number), from 92 to 97. Paraffin and ceresin lower the numbers proportionally.

As the saponification of a wax, especially in presence of much unsaponifiable matter, is slow and difficult, it is well to mix the alcoholic solution with an equal volume of ether which has the property of hastening the action of the alkali. Some prefer to saponify a large weight of the wax by a concentrated aqueous solution of caustic alkali, precipitate the mixed constituent acids and unsaponifiable matter by acidification with a mineral acid, filter and dry the mixture; then weigh a suitable portion of this "decomposed wax," dissolve in neutral alcohol, and titrate the acid by standard alkali.

In determining the *Hehner number* it must be remembered that the fatty acids are mixed with considerable unsaponifiable matter which must first be extracted by ether.

The *iodine number* is low, about 11 to 12; after bleaching by permanganate or bichromate, only 5 to 8.

For the determination of *paraffin* or *ceresin* in commercial wax the following have been proposed.

1. The wax is saponified by a concentrated alcoholic solution of caustic soda

and the solution evaporated to dryness. The residue is extracted by chloroform in a Soxhlet apparatus, dissolving the paraffin or ceresin and the myricyl alcohol. The chloroformic solution is evaporated to dryness and the residue boiled with acetic anhydride which forms a soluble ester with the myricyl alcohol, while the paraffin floats on the surface and may be separated by filtration and washing with acetic anhydride and water.

2. Another method is based on the insolubility of paraffin in a mixture of ethyl and amyl alcohols at a low temperature, while wax is held in solution. The wax is dissolved in a small quantity of amyl alcohol and the solution mixed with an equal volume of 75 per cent ethyl alcohol. After standing for some hours at 4° or below, the liquid is filtered through a dry paper and the residue washed with a mixture of the alcohols, the temperature being kept as low as possible. The residue is dissolved in ether or gasoline, evaporated to dryness, heated to 125° and weighed.

3. Following the Buisenes, the wax is heated with solid potash-lime to 250° whereupon the alcohols of the wax are decomposed with formation of potash soaps — *e. g.*, $C_{27}H_{55}OH$ (ceryl alcohol) $+ KOH = KC_{27}H_{53}O_2$ (potassium cerotate) $+ 2H_2$; one gram of wax should yield from 53.5 to 57.5 Cc. of hydrogen corresponding to 52.5 to 56.5 per cent of myricyl alcohol. The potash soaps are insoluble in gasoline. The residue is extracted by gasoline, and the solution evaporated leaving a mixture of the hydrocarbons and the paraffin or ceresin. From the weight of the residue can be approximately calculated the proportion (X) of paraffin or ceresin from the formula $X = 100\,\frac{d-b}{a-b}$, where a is the percentage of hydrocarbon in the adulterant; b, the percentage of hydrocarbons in pure wax; and d, the percentage of the residue from the evaporation. Where the adulterant is ceresin or paraffin, a is taken to equal 100, and b about 13.5.

Stearic acid separates when the wax is dissolved in ten times its weight of hot 80 per cent alcohol, the solution cooled and filtered from the cerotic acid, then diluted with a large proportion of water.

SOAPS.

A soap may be described as a compound of a metal with one or more fatty or resin acids, but in popular use the term without qualification has reference to combinations of the fixed alkalies with stearic, oleic, palmitic, or resin acids.

The soaps of commerce are hydrous compounds of soda with the above named acids that do not retain, or but partially, the glycerol formed during the saponification. As associates may be found free sodium carbonate or hydrate, unsaponified fat, and fatty acids, and in toilet soaps, odoriferous principles in minute amounts. Other substances of the most varied nature may have been incorporated during the manufacture to confer some detergent or medicinal quality, or as adulterants or make-weights. The most common are the alkali carbonates, powdered sand or kieselguhr, borax, whiting, sugar, sulfur, etc.

According to the special fats used for stock will the characteristics of the resulting soap be modified. Tallow furnishes a very hard product requiring but little salt for precipitation; palm oil is easily saponified, gives a good hard soap, and is much used in admixture with tallow; cottonseed oil requires a weak lye for saponification, but is difficult to salt out and gives a comparatively soft soap, hence it is always mixed with other stock; the cheaper grades of olive oil are the best basis for textile soaps, the curd being medium hard and the solution remaining liquid at ordinary temperatures even when very concentrated; cocoanut oil requires a concentrated lye but readily saponifies in the cold, though from the liability of the product to become rancid, other stock is mixed with it; low-grade linseed oil gives a soft inferior soap and is seldom used; oleic acid (a waste product), is usually boiled with sodium carbonate instead of the more costly hydrate.

The common soaps, when pure, are readily and completely soluble in hot alcohol, though but slightly soluble in ether, potassium oleate more readily than the stearate. Soap dissolves in cold water but slowly, but in a moderate quantity of hot water passes to a clear solution that becomes a soft mass on cooling. On diluting an aqueous solution with a large proportion of water hydrolysis ensues, the soap partially decomposing to acid and alkaline compounds that may be separated by dialysis, the latter permeating the membrane. It is said that the cleansing properties of soap are due in part to this decomposition.

The specific gravity is above that of water though so near to it that a 'floating soap' is easily made by incorporating air or carbonic acid gas during manufacture.

A technical analysis should comprise the water, fatty acids and alkali both free and combined, unsaponified oil, adulterants and fillers, coloring matter, and medicaments if any. The amount of perfume oils is usually too small for determination.

Water. The loss in weight on drying is due to water plus any alcohol or other volatile matter. Thin shavings cut from the interior of a bar are heated, at first gently to avoid melting, then at 105° to constant weight—

several hours may be required for complete desiccation. The results are always a little low from the tendency of the surface of the soap to dry to a horny skin impenetrable by the moisture of the interior.

A better method is to melt the sample in a tared dish and compound with double the weight of alcohol; when the mass becomes homogeneous an equal weight of dry sand is stirred in and the mixture evaporated to dryness on the water bath. The disintegrated residue is moistened with absolute alcohol, evaporated, and dried at 100° to 105°.

A more rapid scheme is to tare a porcelain dish and short glass rod with flattened end; the soap shavings are introduced with some gasoline and triturated to a paste, this heated to 105° to constant weight.

Probably the most accurate method is to dry the shavings at 110° to 115° in a current of some dry gas and absorb the water in weighed calcium chloride tubes.

Unsaponified fat is extracted from the dried soap by dry ether or gasoline in a Soxhlet's apparatus (page 53). The fats, with any other matter soluble in ether, is left on evaporation of the solution and should be examined qualitatively.

Insoluble matter remains when the residue from the ether extraction is treated with hot water and filtered. A residue will likely be sand, silica, pumice, talc, etc., and may be further separated if needful, though its nature will generally be disclosed by inspection with a lens.

Fatty acids. The filtrate is acidified by addition of a known volume of standard sulfuric acid. If the fatty acids are not to be further examined filtration may be dispensed with by the addition of a weighed lump of ceresin or stearic acid before acidulation; on cooling the acidified liquid the solidified disk of fatty acids and ceresin may be lifted out, rinsed and weighed. Otherwise the liquid is heated until the layers are clear, filtered through a wet paper, and the filter washed with hot water.

A. In the filtrate are sodium sulfate, the excess of sulfuric acid, any glycerol that may have been in the soap, and possibly a small amount of dissolved fatty acids assumed to be caprylic. It is titrated back by decinormal alkali and methyl-orange to find the excess of sulfuric acid. From the difference is calculated the *total alkali* of the soap. Phenol-phthalein is now added and the soluble fatty acids neutralized by titrating with decinormal alkali.

The liquid is evaporated at a gentle heat to a small bulk and tested for *glycerol;* if found, a large weight of soap is dissolved in water, acidified, the liberated fatty acids filtered off, and the glycerol determined in the filtrate.

B. The fatty and perhaps rosin acids on the filter are dried and weighed, then dissolved in hot neutral alcohol and titrated by decinormal alkali and phenol-phthalein. A residue insoluble in alcohol may be silicic acid coming from water-glass in the soap. The solution of soap is now ready for a determination of resin acids if contained (page 473).

Since the neutralizing power of the mixed fatty acids varies with their respective proportions, the empirical titre of the standard alkali is best found against a suitable quantity of the dried fatty or resin acids prepared by decomposing a large weight of the aqueous solution of the soap by acid and filtering. But if the nature of the soap stock used in the manufacture of the brand under analysis is known, the titre may fairly be calculated from the alkalimetric strength.

A rapid method for a determination of the fatty acids only, useful for checking the manufacture of 'run soaps' is due to Walsh. He dissolves the soap in hot water and pours the solution into a separatory funnel. After decom-

posing with a fair excess of sulfuric acid, the funnel is cooled under the water-tap and ether added to dissolve the liberated fatty acids. The subnatant liquid is run off and the ether washed with saturated brine until the excess of sulfuric acid is gone. The ethereal solution is then diluted with alcohol and titrated by standard alkali and phenol-phthalein. In a modification of this scheme the ether solution is evaporated and the residue weighed, it consisting of fatty acids and unsaponified fat.

The nature of the soap-stock, if unknown, may be deduced from the constants of the fatty acids, sometimes with reasonable assurance. The color, consistency, odor (in an unscented soap), etc., may also afford clues.

The direct separation of the mixed fatty acids is a matter of difficulty and cannot be relied on as giving more than approximate results.*

For the determination in the mixed acids of those liquid at ordinary temperatures (oleic, linoleic and their homologues) and solid (stearic, palmitic, etc.), the Muter and DeKoninck process applies the solubility in ether of the lead compounds of the liquid acids as against the comparative insolubility of those of the solid. The separation is made by precipitating the hot neutral aqueous solution of their potash soaps by lead acetate; the lead soaps are washed with hot water, dried, and extracted by hot ether. The ethereal solution of the liquid acid soaps (here usually lead oleate) is treated with hydrochloric acid to decompose the lead oleate, forming lead chloride which passes into the aqueous solution, and free oleic acid which remains in the ethereal layer. The latter is decanted, washed with water to remove any dissolved hydrochloric acid, then titrated by standard alkali; or the weight of iodine absorbed (page 455) may be found. The lead compounds of the solid fatty acids, left after the ether extraction, are decomposed by hydrochloric acid, and the liberated fatty acids determined as above. A special apparatus is recommended for the analysis. The results are only fair at best, and should the ratio of oleic to stearic acid be small, the lead compound of the former is not completely extracted by ether.

Roese, following Varrentrapp, treats the mixed fatty acids with ether and lead protoxide, and allows the solution to stand for a day or two with occasional shaking up, then dilutes to a definite volume and filters. An aliquot part of the filtrate is evaporated, and the residual lead compounds of the liquid acids dried in a current of carbon dioxide and weighed, then decomposed by sulfuric acid and alcohol, the fatty acids passing into solution, the lead sulfate weighed and calculated to lead oxide; the difference in weight is the weight of the anhydrides of the liquid fatty acids. The molecular weights and the approximate percentage of each fatty acid can be calculated — since only normal compounds are formed — from the combining ratio with lead oxide and a determination of another constant, according to the formulae on page 157.

The residue of the lead compounds of the solid fatty acids plus the excess of litharge is dried and weighed. The lead oxide in the residue is determined as before and the difference in weight is that of the solid fatty acids.

Other modifications are by Fahrsteiner who separates the lead compounds by cold benzene, and by Halphen who obtains the zinc salts of the mixed acids and separates by carbon disulfide.

Hazura states that when treated in dilute solution with alkaline potassium permanganate, the hydroxy-group is added to the unsaturated fatty acids only; thus, oleic acid ($C_{18}H_{34}O_2$) is converted to dihydroxystearic acid ($C_{18}H_{34}O_2 \cdot (OH)_2$) insoluble in water and but sparingly soluble in ether, but readily in hot alcohol.

* Brannt, Oils and Fats, 78; Analyst, 1898—285; Journ. Amer. Chem. Socy. 1895—289.

The soaps in dilute solution are digested for a short time with permanganate solution, filtered from precipitated manganic oxide and the filtrate acidified by hydrochloric acid. The precipitated fatty acids are extracted by ether which leaves the hydroxylated acids behind. If the oxidation be carried too far, products other than the hydroxy-acids are formed.

According to Twitchell unsaturated fatty acids react with concentrated sulfuric acid to form additive compounds that are insoluble in petroleum ether. Saturated acids do not combine with sulfuric acid.

Other methods are by fractional fusion and expression, fractional precipitation by magnesium acetate from an alcoholic solution, extraction of the barium compounds, etc.

Free alkali. A portion of the soap is dried in air free from carbon dioxide and the unsaponified matter washed out by ether; the residue is dissolved in hot neutral strong alcohol, and titrated by deci-normal sulfuric acid. Insoluble in alcohol are sodium carbonate, silicate and borate, sugar, starch and other matters, to be further examined.

The determination of free alkali is important in a toilet or medicinal soap. Those made by the cold process (saponification below a boiling temperature) are apt to contain both free alkali and unsaponified fat, and on dissolving in alcohol or water the two may unite to some extent. As it is always safer to assume that both are contained in a sample, the method adopted must provide for the removal of one or the other before the soap is dissolved; in the above the fat is extracted by ether.

If the absence of free fat in the soap is assured, simpler methods can be used. Wilson calls free alkali the difference between the total alkali and that calculated to neutralize the fatty acids, both determined by analysis. Hope applies the insolubility of sodium carbonate in strong alcohol; he dissolves the dried soap in hot absolute alcohol, adds phenol-phthalein, and passes a few bubbles of carbon dioxide until the solution becomes colorless (to convert the caustic alkali to carbonate), then filters and washes with hot strong alcohol. In the residue is all the free alkali as carbonate with other insoluble matter, and may be titrated directly by weak standard acid and methyl orange.

A separation based on the insolubility of soap in strong brine is possible. The concentrated aqueous soap solution is precipitated by saturation with sodium chloride, filtered and washed with saturated brine; the precipitate is redissolved in water and the precipitation repeated. The united filtrates contain the free alkali and are to be titrated by standard acid; the free fatty acids are in the precipitate and may be extracted by alcohol and titrated by standard alkali and phenol-phthalein.

Low determines sodium carbonate by dissolving the soap in hot alcohol, running in more than enough standard hydrochloric acid to decompose the carbonate, boiling to expel carbonic acid, and titrating back by equivalent sodium hydrate and phenol-phthalein. The difference in volume is that of the hydrochloric acid corresponding to the carbonate of sodium. There is now in solution a neutral soap plus sodium chloride, etc. The combined alkali is titrated by standard hydrochloric acid and *lacmoid;* the liquid remains clear since fatty acids are soluble in alcohol.

If a determination of the fatty acids is wanted, they are neutralized by sodium hydrate, the soap evaporated to dryness, dissolved in water, acidified and filtered. The fatty acids are dissolved in alcohol, neutralized by titration with sodium hydrate (free from potassium hydrate), evaporated to dryness, and the soap weighed. The amount of sodium oxide therein is calculated from the titration; the difference is fatty acids.

The *combined alkali* is understood to be the difference between the total alkali and that in the free state or as carbonate, plus any that is combined with acids other than fatty or resin acids. If there is no free fatty acid or fat in a soap and the composition of the original fat is known, the combined alkali can be calculated from the weight of fatty acids found. A direct determination can be made by dissolving the soap in absolute alcohol, filtering, evaporating the filtrate to dryness, and weighing the residue; then igniting to burn the fatty acids, and titrating the residue of carbonate of sodium by a standard acid. The difference between the alkali as calculated from the titration and the weight of the residue from evaporation is the fatty anhydrides, which multiplied by 1.03 gives the corresponding fatty acids.

Of the more common admixtures and adulterations, *sugar* may be determined by dissolving the soap in water, liberating the fatty acids by heating with dilute hydrochloric acid, filtering and determining the invertose in the filtrate, but here the optical activity of other soluble matters in the soap may increase the reading. Wilson precipitates the fatty acids from an aqueous solution of soap by a saturated solution of magnesium sulfate, filters, evaporates the faintly alkaline filtrate, acidifies and clarifies by lead acetate and alumina cream, and polarizes.

Another plan is to treat the aqueous solution of the soap with slaked lime and a quantity of sand and evaporate to dryness. A pasty grease remains on cooling containing the sugar as calcium saccharate, which is to be treated with a mixture of alcohol and ether to dissolve out the glycerol. The residue is boiled with dilute sulfuric acid to decompose the saccharate and invert the sugar; the latter is then determined by Fehlings solution or the saccharimeter.

Sand and like insoluble bodies are left when the soap is dissolved in hot water and may be dried and weighed; amorphous silica can be dissolved out by a solution of caustic alkali. *Sodium silicate* remains when a soap is dissolved in alcohol, and may be decomposed by hydrochloric acid and the silica determined as usual. It is said that sodium silicate does not react alkaline to phenol-phthalein in a soap containing less than 15 per cent of this compound.*

The analysis of metallic-fatty-acid compounds (other than of the alkali metals), known as plasters, greases, etc., proceeds along the same lines as that for an ordinary soap, but being insoluble in water, the fatty acids are liberated by boiling at once with dilute hydrochloric acid. After filtering, the fatty acids are neutralized, and any saponifiable oils or fats hydrolyzed by potassium hydrate, and the unsaponifiable matter extracted from the soap by ether. The determination of the metallic base of the soap usually presents no difficulties.

Resin anhydrides. The resins are a class of bodies whose exact composition has not as yet been fully established. Common colophony, or shortly rosin, is the residue left when the turpentine has been distilled from the exudation of the Georgia pine, and consists mainly of an acid (abietic, $C_{19}H_{28}O_2$?) or mixture of acids with certain hydrocarbons. When the acid is neutralized by sodium hydrate a rosin soap is formed which is soluble in hot water and in alcohol but insoluble in ether, and presents many of the characteristics of a fatty acid soap.

In the analysis of a soap containing rosin acids the problem is to separate them from the fatty acids in the mixture obtained on decomposition of the soap with a mineral acid. Four methods will be outlined.

1. Twichell's † Of the four this is generally acknowledged the superior. It

* Analyst, 1896—72.

† Journ. Anal. Appl. Chem. 1891—379.

is based on the principle that the fatty acids are converted into ethylic esters when treated with hydrochloric acid in alcohol solution, while under these circumstances the resin acids are unaffected and separate as such.

If a commercial soap is under examination, it is dissolved in water and acidified, and the mixture of fatty and rosin acids separated from the solution and dried. A few grams of the mixture is weighed and dissolved in absolute alcohol and a current of dry hydrochloric acid passed through the cold solution to saturation. On diluting with water and boiling, the ethers and resin acids float, and after cooling the solution, may be dissolved in ether. The aqueous solution is drawn off from the ethereal in a separatory funnel and the latter washed with water.

The ether solution is now diluted with alcohol and the resin acids titrated by standard sodium hydrate, the ethers not interfering. The mean combining weight of the acids of rosin may be taken as 346. The percentage of fatty acids is found from the difference on titrating a portion of the mixed acids by alkali.

Or the resin acids may be determined gravimetrically by dissolving the ethers and resin acids in gasoline and separating from the aqueous solution. On treating the former with water and potassium hydrate the acids are neutralized and pass into the aqueous solution while the ethers remain in the gasoline. The soap solution is decanted, decomposed by acid, and the resin acids filtered and weighed.

2. Gladding's.* The silver salts of the resin acids are soluble in ether while the silver salts of the fatty acids are insoluble. The mixture of fatty and resin acids is dissolved in a small quantity of alcohol, the solution neutralized by potassium hydrate, and diluted to a known volume with ether. Finely powdered silver nitrate is stirred in and the mixture agitated, when the silver salts of the fatty acids precipitate in flocks. One-half of the clear liquid is drawn off and the silver resinate decomposed by hydrochloric acid, chloride of silver precipitating. From the filtrate the resin acids are recovered by evaporation. The silver salts of the fatty acids may be suspended in water and decomposed by hydrochloric acid and the fatty acids determined.

Bouley † dispenses with the isolation of the mixed acids by compounding the aqueous solution of the soap with silver nitrate, evaporating to dryness, and dissolving out the silver resinate by extraction with ether in a continuous percolation apparatus.

3. Barfoed's. The sodium resinates are soluble in a mixture of anhydrous alcohol and ether while the fatty acid soaps are insoluble. The mixed acids are dried and weighed, neutralized by sodium hydrate, the solution evaporated to dryness and the residue powdered, then heated with absolute alcohol; on the addition of ether the fatty acids are precipitated and the resin acids go into solution. The liquid is made up to a definite volume and an aliquot part of the clear supernatant liquid withdrawn, evaporated to dryness, the residue dissolved in water and the resin acids precipitated by a mineral acid. Subtracting their weight from that of the mixture gives the weight of the fatty acids. The separation is not as sharp as has been claimed, especially where one of the fatty acids is oleic.

A similar approximate separation is by the process of Jean-Remont. The mixed acids are combined with barium and the baryta soaps extracted by hot 85 per cent alcohol which dissolves only the baryta resinates.

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* Journ. Socy. Dyers & Col. 1895—86.

† Journ. Socy. Dyers & Col. 1892—82.

4. Cornette's method depends on the insolubility of the sodium compounds of the higher fatty acids in a concentrated solution of sodium chloride, the corresponding resinates being freely soluble. To the solution of the fatty acids in a little alcohol are added sodium hydrate to neutralization and after cooling, strong brine, and the precipitate of the soaps of the fatty acids filtered and washed with salt solution. From the filtrate the resin acids are precipitated by a mineral acid; the fatty acid soaps may also be decomposed in the same way.*

* Chem Zeit. 1897—25.

MILK — BUTTER.

The lacteal secretion of mammals is a white liquid composed of globules of fat suspended in a fluid known as milk-plasma, serum, or whey.

The following are analyses of the milks of various animals.

	Water.	Total solids.	Fat.	Casein.	Milk-sugar.	Ash.	Albumin.
Human.....	88.19	11.81	3.78	1.00	6.22	.31	.56
Cow.....	87.23	12.77	3.66	3.02	4.85	.71	.53
Goat.....	86.85	13.52	4.34	2.53	3.78	.65	...
Ewe.....	83.30	16.60	6.05	5.73	3.96	.68	...
Ass.....	89.01	10.99	1.85	3.57	5.05	...	...
Mare.....	90.45	9.55	1.31	2.53	5.42	.29	...
Buffalo.....	80.64	19.36	8.45	4.25	4.51	.85	...
Camel.....	86.34	13.66	2.90	3.67	5.78	.66	...
Sow.....	81.80	18.20	6.00	5.30	6.07	.83	...
Elephant.....	66.70	33.30	22.07	3.21	7.39	.63	...

Cows milk is essentially a solution of milk-sugar, casein, albumin, mineral matter and small quantities of various organic bodies, holding in suspension innumerable minute globules of a fat. The quantitative composition varies considerably, marked differences resulting from the breed of the cows, kind and amount of feed, the season of the year, time and manner of milking, etc., hence legal limits as to the percentage of the different constituents in salable milk are only to be established from data furnished by a large number of samples known to be unsophisticated.

Richmond* has published the following figures as the averages of 172,000 samples of new cows-milk received at the Aylesbury Dairies in England: specific gravity at 60° Fahr., 1.03215; total solids, 12.86 per cent, consisting of fat, 4.02, and of solids-not-fat, 8.84. In fourteen years the yearly averages showed extreme differences in specific gravity of .0008; of total solids, .40; of fat, .38; and of solids-not-fat, .20 per cent. Of the milk believed to be genuine, that with less than 8.3 per cent of solids-not-fat was only .059 per cent of the total receipts, and under 8.1, only .01 per cent. Faber states that the results of about 50,000 analyses show the solids-not-fat to be an almost constant number, viz., 8.7 to 8.8 per cent.

The legal minimum in many of the United States is a specific gravity of 1.029; total solids, not less than 12 per cent; and fat not less than 3 per cent. But Van Slyke believes that genuine milk not infrequently falls below the two latter requirements.

The proximate analysis of a milk for the major constituents is not difficult. The number of constituents to be determined depends on the object for which the analysis is prosecuted; usually the investigation is carried only so far as will suffice to assure the chemist that the sample has or has not been sophisti-

* Analyst, 1897—98 and 1898—90.

cated. Some authorities urge that the chemical analysis be always followed by a microscopical examination, and a search for disease germs when warranted by an unhealthy condition of the cow.

Where an immediate examination of a sample of milk is not practicable, decomposition can be prevented for some time by the addition of a trace of a preservative or germicide. Special precautions are required in the analysis of a milk altered by fermentation.

On account of the considerable difference between the specific gravities of the fat and whey, the portions for analysis should be drawn out only after thorough agitation of the original quantity. The portions for the various determinations may be weighed; or more conveniently measured from a pipette, and the weight calculated from the specific gravity of the sample. Pipettes are on sale graduated to deliver certain weights based on the average specific gravity of milk.

Water. The average percentage is about 88.75. The determination is most accurately made by evaporating in vacuo a small volume of the milk and absorbing the distillate in a tared chloride of calcium tube, but the practical value of the determination does not justify so elaborate a process. With few exceptions, the content of water is found (1), by the loss in weight on evaporation of the milk to dryness; (2), calculated from the specific gravity of the milk; or (3), in a complete analysis, by difference.

The usual method is to tare a flat-bottomed platinum dish, introduce five grams or five cubic centimeters of milk, evaporate to dryness on the water-bath and heat the residual solids in an air bath to 100°; the loss in weight is water. The residue can be used for the determination of fat or other constituents if desired.

Practically milk is adulterated only by watering, skimming off the cream, or both. It is somewhat difficult to distinguish between a genuine milk low in fat and one from which part of the fat has been abstracted. Richmond calculates the water of dilution by uniting the percentage of fat found by analysis to the specific gravity (water = 1000), and deducting 1000 from the sum. The remainder in the case of normal milk is, on an average, 36, but taking 34.5 as a safer basis, the proportion stands 34.5 : remainder : : 100 : percentage of genuine milk in the sample. Thus a milk having a specific gravity of 1029.2 and containing 3.27 per cent of fat, would appear to contain only 94.1 per cent of genuine milk plus 5.9 of added water. This on the assumption that the addition of water reduces the specific gravity and percentage of fat in the same proportion.

(1) When the sample has simply been diluted with water the proportion of fat and solids-not-fat are correspondingly reduced, and the percentage of added water is calculated from the formula $X = \frac{S' W}{S} - W'$, where X is the added water; W, the percentage of water in the sample; S, the solids not fat; and W' and S', the minimum averages of water and solids-not-fat in genuine milk. An allowance must be made for the solid constituents of the added water if it be very hard.

(2) For skim milk or separated milk the amount of fat abstracted, Y, is obtained from the formula $Y = f' - \frac{S' f}{S}$ where f is the percentage of fat in the sample, and S of the solids-not-fat; and f' and S', the minimum average of fat and solids-not-fat in genuine milk. The fat removed times 1.54 is approximately the percentage of cream removed.

Should the water of dilution contain nitrates, absent from genuine milk, one of the colorimetric methods used in water analysis may be applied to the coagulated and filtered sample.

Total solids. The total solid matter may be calculated with fair accuracy from the specific gravity. This is a resultant of two factors, the proportion of fat, which is lighter than water, and of the solids-not-fat, which are heavier; and therefore as the fat is greater or the solids-not-fat less, the lower the specific gravity, and vice versa. Hence the possibility of removing part of the fat by skimming, then lowering the specific gravity again to the normal by pure water — a common practice of dairymen in former times when the gravity alone was the criterion of unadulterated milk.

The density of normal milks at 60° Fahr. ranges from 1.020 to 1.035, though only a small proportion fall outside of the limits of 1.028 to 1.034, and when the milks of several cows are mixed, is fairly constant at 1.030 to 1.032; the legal minimum in some States is 1.029. Any method of observation may be employed, the simplest being the lactometer, a specially graduated hydrometer with a thermometer inclosed. As read by this instrument, the mean density of several thousand samples was 1.032. The Quevenne lactometer is graduated in degrees of specific gravity, the integer (1) and first decimal (0) being omitted on the scale for want of space. It is usually graduated from 20 to 40.

Although combined skimming and watering may fail of detection by a density determination alone, if the fat also is found the total solids may be calculated with fair certainty by the formula of Hehner and Richmond,* $T = \frac{262.5\,(D-1)}{D} + 1.2\,F$; where T represents the total solids D, the specific gravity (water = 1) and F, the fat.

The direct determination of the total solids is done by evaporating a small volume of the milk in a flat-bottomed dish on the water bath, and drying the residue at 100° to constant weight. Davenport† directs five grams in a dish of 2.5 inches diameter with a flat bottom rounding up into the sides, as in this form the residue is left in a uniformly thin layer readily parting with the last traces of water. Blyth‡ finds that evaporation in glass or porcelain dishes invariably yields slightly higher weights of residue than in platinum, due perhaps to the shape of the vessels and consequent variations in the thickness of the film, or to the lower temperature of drying from the inferior conductivity of glass for heat. The water passes off more quickly when the evaporation is done in vacuo.

Instead of evaporating the milk in a dish, some prefer to soak it up in sand or asbestos, thereby extending the surface and facilitating the removal of water. Babcock proposes a perforated metal vase filled with flocculent asbestos, the residue being left in a form suitable for the extraction of the fat.

The solids-not-fat are milk-sugar, proteids (principally casein), and inorganic salts. Traces of citric acid (about .1 per cent) and various organic bodies are also contained. The solids-not-fat rarely fall below 8.5 in a normal milk, and are practically constant at 8.75.

Ash. The ash of genuine milk is composed principally of the alkalies and calcium united with phosphoric acid and chlorine, but owing to changes induced on combustion of the organic matter of the residue from evaporation, the ash

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* Analyst, 1898—2.

† Journ. Anal. Chem. 1889—309.

‡ Blyth, Foods, 268.

does not represent exactly the salts as they existed in the milk. About 80 per cent of the ash is soluble in water, the solution reacting neutral, and the remainder soluble in dilute hydrochloric acid. Carbonates and borates are absent.

However low in solids-not-fat a sample of genuine milk may be, it yields never less than .7 per cent of ash, while the majority of abnormal samples leave an unusually high ash with an unduly large proportion of chlorine. Watering a milk reduces the ash almost proportionally if the water be fairly pure. Richmond regards watering as practically proved if the weight of solids-not-fat is exceptionally low, and the ash, though of normal weight, has an alkaline reaction and contains sulfates, or of which more than 30 per cent is soluble in water.

The determination is made by calcining the residue from evaporation in a platinum dish until the inorganic matter is fairly white. Owing to the ready fusibility of some of the constituents, the dish is never allowed to become heated above dull redness. The volume of milk evaporated for the ash determination should be moderate — say 25 Cc. — as with a vessel of the usual size so much carbon separates from a bulky residue on ignition that its combustion increases the heat to above the melting point of the ash. To prevent loss of sulfur and phosphorus in organic combinations, the milk may be acidified by nitric acid before evaporation, this however converting sodium chloride to the nitrate.

Acidity. Immediately after leaving the cow, the reaction of milk is amphogenous, said to be due to calcium phosphate. But shortly the reaction turns decidedly acid from the conversion of milk-sugar to lactic acid — $C_{12}H_{24}O_{12} = 4HC_3H_5O_3$.

For a determination, the carbon dioxide is removed from the milk by dilution with hot water and boiling, then the liquid titrated by decinormal alkali and phenol-phthalein. The result is expressed in terms of lactic acid.

Lactic acid may be determined gravimetrically by combining it with lead to form lead lactate, this salt soluble in acid and neutral solutions, but precipitated from an ammoniacal solution containing alcohol. The lactic acid and fat are extracted by ether from the residue left on evaporating the milk. The ether solution is mixed with water and the ether driven off by heating, when the fat separates and may be filtered off. The filtrate is treated with lead acetate, filtered from any precipitate of carbonate, etc., and mixed with alcohol and ammonia. The precipitate is washed with alcohol, dried and weighed as $3PbO.2(C_3H_6O_3)$. If desired the precipitate may be suspended in water, the lead thrown down by hydrogen sulfide, and the lactic acid determined in the filtrate.

In a modification of the above, the milk is evaporated to dryness and the fat extracted by carbon disulfide. The residue is treated with oxalic acid and water, then with lead hydroxide, and filtered. The filtrate contains lead lactate which may be precipitated and weighed, or converted to zinc lactate by digestion with zinc oxide and the product crystallized.

Another method applies the property of ether to extract from milk both fat and lactic acid, and of carbon disulfide to extract fat only. Equal volumes of milk are extracted by these reagents, the two solutions evaporated, and the residues weighed; the difference between the weights is lactic acid.

Fat. The fat of cows milk is a glyceride yielding fatty acids and glycerol on saponification, but is distinguished from other animal fats by containing a notable proportion of butyrin and its analogues.

The fat is obviously the constituent of most importance to the consumer,

and many methods have been contrived for its determination. They may be divided into four classes:

1. Wherein the fat globules are segregated or collected to a liquid floating on the whey, the volume measured, and the weight calculated.

2. Wherein the fat is extracted directly from the milk by an organic solvent, the solution evaporated, and the residual fat weighed or its weight computed from data given by measuring some physical property of the solution.

3. Wherein the water is removed from the milk by evaporation or absorption and the fat extracted from the total solids by an organic solvent, yielding it on evaporation.

4. Approximately, by some physical characteristic of the milk.

1. The milk is allowed to stand for 24 hours in a tall graduated jar until the globules have risen to the surface, when the volume of the cream is read. The 'creamometer' holds 100 volumes of milk and is graduated from zero at the top down to 20 volumes, the cream rising to compass ordinarily from 11 to 13 divisions. The method is practically obsolete, on account of its slowness, that the fats of milks from different breeds and individual cows do not separate uniformly, and that the temperature and time of repose largely affects the extent of the separation.

Marchand's lactobutyrometer is a specially graduated test-tube about twelve inches long by one-half inch diameter, divided from 20 to 30 Cc. into tenths of a Cc. Ten Cc. of milk is introduced with enough potassium hydrate to dissolve the casein; then ten Cc. of ether is added, which on shaking extracts the fat. Finally strong alcohol is poured in and the mixture well shaken. The alcohol throws out the fat from the ethereal solution, and on standing, the fat collects above the layers of serum and alcohol-ether, where its volume may be read by the graduations on the tube, one Cc. corresponding to .233 gram of fat. A correction is made for the constant quantity of fat retained in solution by the ether-alcohol.

As the adulteration of the milk has been so extensively carried on, systematic examination becomes a necessity for the protection of the public. Affording a means for the rapid division of a number of samples into two classes, the probably genuine and the doubtful or probably adulterated, the processes described below have made possible an effective control of the quality of the supply to cities and dairies. The processes are very rapid and a large number of samples can be carried through in one period. The results are accurate enough for the purpose of differentiation and are as a rule reliable, yet it is advised that any abnormal showing on which much depends be checked by a gravimetric method.

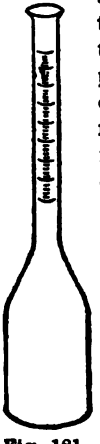

Fig. 181.

The separation and measuring of the fat is done in a small cylindrical flask, Fig. 181, with a long narrow neck graduated into cubic centimeters or directly into percentages and tenths of fat. A measured volume of the milk is run into the flask followed by the reagent. The flask containing the hot mixture is laid in a centrifuge (page 86) and whirled for a few minutes, lying meantime in a horizontal radial position mouth inwards. The flask is then removed, the liquid made up to the highest division with hot water, and again centrifuged for a minute. The entire mass of the fat will now have risen to lie between some two of the divisions where its volume may be read.

A number of modifications of the flask, reagent, and details of operating

have been proposed. The original device of Laval known as the lactocrite has been largely superseded by the apparatus of Babcock, Leffman and Beam, Gruber and others.

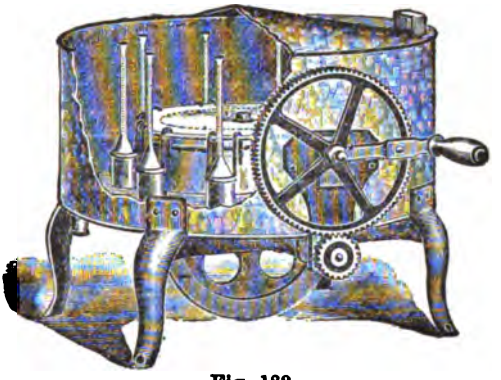

Fig. 182.

Babcock directs the use of 17.6 Cc. of milk, equal practically to 18 grams, with an equal volume of sulfuric acid. The mixture becomes dark in color and very hot, and the casein is nearly or completely dissolved. The flasks and centrifugal machine are shown in Fig. 182. Leffman and Beam's flasks are graduated on the neck directly to tenths of one per cent V/V of the fat. Their formula for the mixture is 15 Cc. of milk with 9 Cc. of concentrated sulfuric acid, 1.5 Cc. of concentrated hydrochloric acid, and 1.5 Cc. of amyl alcohol, the two latter aiding to a sharp separation of the fat. Afterward the mixture is diluted with a hot mixture of one volume of sulfuric acid with two volumes of water, then whirled for two minutes.

Gruber's directions call for ten Cc. of milk, ten Cc. of sulfuric acid, and one of amyl alcohol; that of Stokes is but slightly different. Patrick heats with a mixture of nine parts of concentrated acetic acid, five of sulfuric acid, and two of hydrochloric. Leze heats one part of milk with two of concentrated hydrochloric acid until the liquor turns brown, then dilute ammonia until clear, and finally dilutes with hot water. He finds the specific gravity of the fat liberated in this way to be nearly .900. All the above modifications act or are supposed to act to advantage for the segregation of all the fat to a clear homogeneous liquid.

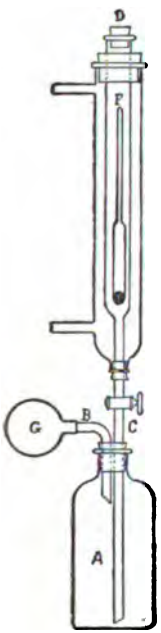

Fig. 183.

Instead of collecting and measuring the fat itself, some would operate on the fatty acids therefrom. In the methods of Short and Thoerner, the milk-fat is saponified by potassium and sodium hydrates, which on long heating also dissolve the casein and albumin. The soap is decomposed by sulfuric, or sulfuric and acetic acids, and the fatty acids floated by a centrifuge and measured, the volume being to that of fat as 100 to 87.

2. In the areometric method of Soxhlet the fat is extracted by ether from the milk made alkaline by potash. As the fat is in the form of an emulsion the extraction is complete in one operation. Two hundred Cc. of the milk is made alkaline, a known volume of water-saturated ether added, the mixture shaken for a few minutes, and the specific gravity of the ether observed; from the increase in density of the ether is calculated the proportion of fat taken up. The operation is conducted in an apparatus shown in Fig. 183. In the bottle A is fitted a cork through which pass the tube B ending just below it, and C, which can be raised or lowered as desired. The upper end of C is enlarged to a cylinder D containing a delicate areometer F with thermometer inclosed, and surrounded by a water-jacket holding water at 17.5° to keep the temperature of D constant. When the

ethereal solution of the fat has risen to the surface, the tube C is lowered until the lower orifice is just above the surface of the aqueous solution. If now air be blown into B by compressing the rubber bulb G, the ethereal solution is forced up into D where its gravity may be read by the areometer. The increase in gravity is referred to a table drawn up from gravimetric determinations. Wiley* secures a prompt separation of the ether and water solutions by the aid of a centrifuge. The method fails for certain milks.

Cronander proposes to evaporate the ether extract and measure the volume of the molten residual fat.

In the method of Werner Schmid,† ten grams of milk in a graduated test-tube of 50 Cc. capacity is heated to 100° with ten Cc. of concentrated hydrochloric acid, and after cooling, the fat taken up by 30 Cc. of ether. The volume of the ethereal layer is noted, and ten Cc. drawn out with a pipette, evaporated to dryness, and the fat weighed. A safer plan is to extract all the fat by four smaller portions of ether, evaporate the whole and weigh. The method can also be applied to the residue of total solids from evaporation of the milk, by heating it with six to eight Cc. of hydrochloric acid, and transferring the paste to the graduated tube.

Failyer and Willard substitute gasoline for ether in the above, while Gottlieb prefers a mixture of ammonia, alcohol, ether and gasoline.

Liebermann and Szekely emulsify 50 Cc. of milk with five Cc. of potassium hydrate solution sp. gr. .663. To the emulsion is added 50 Cc. of 96 per cent alcohol, and the mixture shaken for several minutes. When the gasoline has separated, 20 Cc. is withdrawn, evaporated in a tared flask, and the residual fat weighed.

In a method due to Wollny, the proportion of fat is estimated from the refractive index of an ethereal solution. The milk is acidified by acetic acid and treated with an alkaline glycerol solution of copper oxide, and one-fifth the volume of water-saturated ether. After brisk agitation, a little of the ether solution is withdrawn and examined in a special form of refractometer. It is claimed that the results are accurate within .1 of one per cent of gravimetric methods.

3. Of the methods wherein the fat is dissolved from the total solids that of Bell is well known, and up to recent times has been extensively employed. Five to ten grams of milk in a flat-bottomed dish is evaporated to dryness on the water bath. The fat is dissolved from the residue by hot ether or like solvent, filtered, the filtrate evaporated to dryness, and the fat weighed. Bell lays stress on the condition of the residue of total solids, advising that it be neither too moist nor too dry, as in either case a little fat remains undissolved. For sour milks, carbon disulfide has the advantage over ether of not dissolving lactic acid.

Instead of dissolving out the fat by ether, Davenport fills the platinum capsule with naptha, allows to boil down to one-half, and decants carefully, repeating the operation three or four times. The residue is dried and reweighed, the fat being the difference. The residue may be used for an ash determination.

But it appears to be conceded by the majority of chemists that the attenuation of the film of total solids as secured in the methods of Bell and his followers is not sufficient to insure the perfect extraction of the fat, the casein and salts enveloping and protecting it from contact with ether. Recognizing this, Kummer‡ would drop about one gram of milk on a tared flat glass plate about

* Journ. Anal. Chem. 1887—124.
† Zeits. anal. 27—464.
‡ Chem. News, 1893—2—1.

three inches in diameter, dry and weigh; then remove the scale to a small thick flask and digest with ether at 100° to 120° Fahr. The flask is cooled, weighed, most of the clear ether solution poured out and the flask reweighed. The solution is then evaporated to dryness on a tared watch-glass and the fat weighed.

To further increase the surface exposure of the total solids, the milk may be absorbed by some porous solid or powder insoluble in ether. Many substances have been named for the purpose — sand, pumice, infusorial earth, precipitated silica, glass-wool or powder, asbestos, sponge, wood fiber or pulp, lint, paper, cloth, etc. Obviously, refractory inorganic bodies have an advantage in that they may be deprived of ether-soluble organic matter by simple ignition, also that they are less hygroscopic and that the residue from the fat extraction may be used for a determination of ash; however, they are much less used than organic absorbents.

In Adams' method, official in England, a strip of filter paper, about 22 inches long by 2.5 inches broad, is rolled into a tight coil. On one end of the coil is dropped from a pipette five cubic centimeters of milk. It is then dried at steam heat and the fat extracted by ether in a Soxhlet or like apparatus. The coil must have been previously freed from matter soluble in ether; paper is now on sale that has been so purified by the manufacturer. The ether used for the extraction should be anhydrous and the time of extraction ample.

Thompson, to shorten the time required for drying, would stretch the strip of paper horizontally, drop the milk upon it uniformly from end to end, and dry by radiated heat before coiling up. It is said that where blotting paper is the absorbent, most of the fat remains on or near the surface and is easily extracted.

To dispense altogether with evaporation of the water it has been proposed to soak up the milk in recently ignited calcium sulfate or anhydrous copper sulfate. After grinding up the mixture with sand the fat may be extracted by ether or gasoline.

Other processes direct to compound the milk with certain precipitants, such as copper sulfate or calcium phosphate in acetic acid, which throw down the proteids inclosing the fat mechanically. The precipitate is filtered off, dried, and extracted by ether. Greater accuracy is claimed for this class of methods.

The ethereal or gasoline solution of the fat is evaporated in a tared dish, the residue dried at 100° and weighed; or the solvent may be partly or entirely evaporated and the residual fat saponified by a known weight of potassium hydrate in alcohol, then the excess of alkali determined by titration with standard acid, and the weight of fat calculated from the saponification equivalent.

4. The quality of milk may be approximated by various instruments which measure the color or opacity — the opacity, however, is said to be due principally to colloidal casein rather than to fat. The "pioscope" of Heeren is a black rubber disk in the form of a shallow circular well holding a thin layer of milk; for comparison there are painted six sectors of different shades radiating from the well, grading from the white, which matches cream in color, to the darkest marked 'very poor.' But the indications are not very reliable at best.

The viscosity of milk is said to bear a direct relation to the percentage of fat contained.

Hehner and Richmond state that the percentage of fat in a milk bears a

constant ratio to the specific gravity and total solids, viz.: $T - .254G = 1.164\ F$, where T is the percentage of total solids; G, the specific gravity at 15°; and F, the fat.

Proteids. The chief nitrogenous constituent of milk is casein, with a smaller amount of a form of albumin designated as lactalbumin. Minute amounts of several other nitrogenous bodies are believed to accompany these, but the difficulty of isolating them makes their identity somewhat uncertain.

Casein in normal milk varies from 1.8 to 3.5 per cent or more with an average of about 2.5. The density in solution is nearly 1.34; it is supposed to be in a colloidal combination with mineral matters, released on the addition of an acid or acid salt. The proportion of nitrogen contained is about 16 per cent. Albumin ranges from .55 to .86 per cent. It is said that a milk with less than 1.3 parts of fat to one of casein is probably watered.

The relation of the proteids of milk to the other constituents is expressed in Richmond's formula—

$P = 2.8\,T + 2.5\,A - 3.33\,F - .7\dfrac{1000\ D - 1000}{D}$, where P is the percentage of proteids; T, of the total solids; A, of the ash; F, of the fat; and D, the density at 15.5/15.5° (water = 1).

The direct determination of the total nitrogen of a milk includes that of the proteids and other nitrogenous bodies. It is most conveniently made by the Kjeldahl method, which according to Kruessler gives figures corresponding to the Dumas' combustion method, while the Will-Varrentrapp results are always slightly lower. In genuine milk the nitrogen seldom falls below .55 per cent.

In an approximate method the residue of total solids is lixiviated, first by ether to remove fat, then by hot water containing a little acetic acid to remove sugar and salts. The residue of proteids is dried and weighed.

Casein is precipitated from milk by the mineral acids and some of the organic acids and a large number of inorganic salts, but never pure, always retaining some fat, calcium phosphate, etc. The precipitation by acetic acid is assisted by heating or by passing a current of carbonic acid. Of the reagents proposed for the determination are zinc sulfate, which precipitates all proteids except peptones; magnesic sulfate, which leaves most of the nuclein in solution; calcium phosphate in acetic acid, that on neutralization carries down casein mechanically; potassium mercuric iodide in acetic acid; mercuric nitrate; lead acetate; lactic acid; phospho-tungstic acid; alum; etc.

For the precipitation by acetic acid, 10 Cc. of the milk is diluted with 90 Cc. of water at 40°, then acidified by 1.5 Cc. of acetic acid and allowed to stand for five minutes. The precipitate is filtered and washed by decantation, the nitrogen determined and the result multiplied by the factor 6.25 giving the casein. Van Slyke finds that a definite proportion of acetic acid is advisable and that the method is uncertain for milk that has undergone a noticeable change by age. A shorter scheme is to filter the precipitate on a tared paper and extract the fat by ether, then weigh the residue of proteid plus mineral matter; on ignition in an open crucible the casein burns and is determined by the loss in weight.

According to Palm, tannin precipitates all the albuminoids of milk, but the composition of the precipitate is not constant. The tannin may be entirely washed out of the precipitate by ether-alcohol, or the "protein tannate" decomposed by lead acetate and the solution of proteids freed from the excess of lead acetate by hydrogen sulfide.

Copper sulfate added to highly diluted milk, followed by sufficient alkali to

precipitate the copper, throws down casein and albumin as a copper compound of fairly constant composition. A nitrogen determination is preferable to direct weighing. In the filtrate the albumoses may be determined.

For the separate determination of casein and albumin, the former is precipitated by the acetic method, and the albumin coagulated in the filtrate by boiling, or precipitated by saturating the solution with zinc sulfate. Or the casein may be precipitated by mixing the milk with twice its volume of saturated solution of magnesic sulfate, then saturating the mixture with the solid salt; the precipitate is washed with a saturated solution of the reagent. In the filtrate is the albumin, that may be thrown down by phosphotungstic acid or tannin.

Van Slyke* makes three nitrogen determinations by the Kjeldahl process, the first on the milk directly, giving the total nitrogen; the second on the casein precipitated by acetic acid; and the third on the albumin precipitated in the filtrate from the casein. The nitrogen of the other nitrogenous bodies is the difference between the first and the sum of the second and third. The multiplier 6.25 converts the result for nitrogen to that for proteids.

The ratio of the volumes of a solution of albuminoid matter required to decolorize a given volume of a weak standard solution of potassium permangate acidified by sulfuric acid, (1) in the cold, and, (2) at a boiling heat, is termed by Smith "the expression of oxidation capacity". He finds that for cow's milk the ratio is about 1.2 to .5.

Milk-sugar or *lactine*, $C_{12}H_{24}O_{12}.H_2O$, forms hard white crystals. The percentage in milk ranges from 4.25 to 5.20. It is soluble in water and dilute alcohol, and may be separated from casein and inorganic salts by lixiviating the residue left on evaporation of the milk, though never quite completely. An approximate method is to extract the fat by ether from the solids left on evaporating the milk, weigh the residue of milk-sugar, casein and salts, and calcine it. Subtracting the weight of the ash and casein from that of the residue gives the sugar by difference.

The usual methods, however, are (1) by the reduction of a copper salt, and (2) by the polariscope.

(1) One molecule of milk sugar reduces Fehlings solution with the formation of about seven molecules of cuprous oxide. Muter insists on the dilution of the milk to a degree where there is no sensible action of the alkali on the sugar. In all cases it is best to make a parallel determination on pure milk sugar and calculate the results accordingly.

The milk is prepared for the test by removing the fat and proteids. Boiling with acid and filtering will remove both, but to obtain a clear filtrate is often a tedious operation. It is likely that the figures for milk sugar thus obtained are too high, since lacto-peptone, hemialbumose, and coloring pigments left in solution by the acid also react.

Ritthausen† recommends copper sulfate as a precipitant followed by neutralization by potassium hydrate; filtration may be avoided by making up the mixture to a definite volume and drawing out a portion. The filtrate should contain some copper sulfate and not have an alkaline reaction. Gill heats the diluted milk with an emulsion of aluminum hydrate and filters by decantation through a ribbed paper, obtaining a clear filtrate. Palm would evaporate the milk to dryness, extract the fat by gasoline, treat the residue with lead oxide and water, and evaporate to dryness, then lixiviate the residue by water and filter; the filtrate contains the milk sugar plus a little lead oxide.

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* Journ. Amer. Chem. Socy. 1894—714.

† Zeits. angew. 1896—46.

(2) According to Deniges, the rotatory power of anhydrous milk sugar in aqueous solution at a concentration of from four to thirty-six per cent is + 55.3 at 20° Cent. Both casein and albumin are laevo-rotatory.

For clarification, lead acetate is stirred into the milk, the mixture made up to a definite volume, and filtered through a dry paper. Wiley prefers acid mercuric nitrate or potassium mercuric iodide in acetic acid, while Blyth would use copper sulfate or acetic acid, the settling of the precipitate aided by the centrifuge.

Various *other constituents* of milk are found in minute quantities, but their quantitative determination, when practicable, is not often called for. Such are minor proteids, extractive and coloring matters, citric and other organic acids, urea, alcohol, various metals, etc.

The adulteration of milk outside of skimming and watering is but rarely practiced. The use of preservatives, however, appears to be on the increase. The most common of these are boracic and salicylic acids and formaldehyde. Boracic acid is said to increase the acidity to four times the extent of the same quantity added to water, so that milk which neither tastes nor smells sour yet contains over .3 per cent of acid expressed as lactic, is probably adulterated with some preservative, such as boracic acid.

Since so small a quantity of a preservative is needed for the purpose, only a qualitative test is practicable in most cases. Dialysis may sometimes be of service in separating the greater part and allow of a fair colorimetric or other determination.

For cream the methods of analysis are practically the same as for milk, proportionally smaller amounts being taken for the determinations.

BUTTER.

In churning cream, the violent agitation ruptures the membrane enveloping each fat globule, whereupon the fat coalesces to a soft mass inclosing a part of the casein and traces of sugar and the salts of the cream. The butter is pressed to remove some of the water, and a small proportion of salt incorporated as a preservative. Genuine butter is mainly fat, with a variable quantity of water, small amounts of casein, mineral matter and sugar, and traces of lecithin, cholesterol, phytosterol, and coloring matter.

The composition of butter varies quite considerably. The fat ranges between 75 and 90 per cent; the water from 6 to 18; salt from .5 to 6; casein from .5 to 3; and sugar from .1 to 1 per cent. Of 960 samples 90 per cent held between 10 and 15 per cent of water, and 37.5 per cent between 13 and 14 per cent. The melting point is between 29.4° and 34.7° Cent., congealing at 18 to 21°.

It is yet a disputed point as to whether the fat globules of milk are inclosed in a film of proteid.* Storch, from an extended investigation of the subject, concludes that there is an envelope of mucoid substance which forms over 60 per cent of the proteids of butter. The fat of butter is composed of a mixture of the glycerides of the fatty acids oleic, palmitic and stearic (?), common to animal fats, together with a certain proportion of the glycerides of butyric acid and its associates, the latter absent from other animal fats. According to Bell, the molecule of butter-fat, unlike those of other fats (page 240), is made up of the glycerol radical combined with different acid radicals, thus—

$$C_3H_5\left\{\begin{array}{l} O.C_4H_7O \text{ (butyric)} \\ O.C_{16}H_{31}O \text{ (palmitic)} \\ O.C_{18}H_{33}O \text{ (oleic).} \end{array}\right.$$

* Richmond, Dairy Chemistry, 1 *et seq.*

On undisturbed cooling butter-fat separates into about 45.5 per cent of oil and 54.5 per cent of fat solid at ordinary temperatures. Bell states the composition of butter-fat as butyrin 7.01 per cent; caproin, caprylin, and caprin, 2.28; olein, 37.73; and palmitin, stearin, etc., 52.98.

A theory of Johnstone* asserts that: "Butter-fat then becomes a mixture of iso-oleo-palmito-capriate of glycerin, and tri-nondecatoic of glycerin in varying proportions, a compound, complicated triglyceride. * * * Furthermore, genuine butter fats yielding insoluble fatty acids above 85.81 per cent do not contain stearic acid (?) as is generally supposed, but non-decatoic acid, the next higher acid of the series as a glyceride."

Butyrin, $C_3H_5(O.C_4H_7O)_3$, has a specific gravity of 1.052 at 22° Cent. and distills unchanged at 285°. When boiled with an alcoholic solution of an alkali in quantity insufficient for complete saponification, ethyl butyrate, exhaling its characteristic odor, is yielded. Butyric acid, $CH_3.CH_2.CH_2.COOH$, is a colorless liquid boiling at 162°, and of a specific gravity of .958 at 14°. It mixes with water, alcohol, and ether, and readily distills in steam.

The methods of analysis follow to a great extent those for milk. Since the water in butter may be distributed more or less ununiformly, care must be taken that the sample is a representative of the original. As many of the tests for adulteration are made on the fat alone, a large quantity of the butter is melted at a low temperature and filtered from water and curd. It must not be forgotten that in undisturbed cooling from the melted state considerable segregation takes place.

Acidity. According to Duclaux fresh butter contains from .005 to .010 gram of butyric acid per 1000 grams of butter. With age the proportion increases rapidly, until at .080 gram per 1000 a rancid taste is perceptible.† The determination is made in the usual way for oils and fats — stirring the butter in hot neutral alcohol or a mixture of alcohol and ether, and titrating by weak standard alkali and phenol-phthalein. The limit for a salable article is about eight Cc. of decinormal alkali for 100 grams of butter.

Water. A small beaker covered with a watch-glass is weighed and about 25 grams of butter introduced. The beaker is heated in an air-bath to 105° with occasional stirring until no more globules of water can be seen — generally about an hour will suffice. If a second heating results in no material decrease in weight, the loss is put down as water.

Of 1120 English and Continental butters, 81 per cent contained from 11 to 14 per cent of water, and only .8 per cent of the butters contained above 16 per cent. Bell's conclusion that a greater amount than 12 per cent is unnecessary, and over 16 per cent injurious to keeping qualities, is generally concurred in.

Fat. The beaker is again heated until the fat melts, then the liquid filtered through a dry paper into a small tared dish. When all the fat has passed through, the beaker is rinsed and the paper washed with ether or gasoline until the washings leave no traces of fat on evaporation. The ether is distilled from the fat, the dish heated to 100° for a few minutes, and the fat weighed.

Casein. The filter is washed a few times with hot water containing a few drops of acetic acid, receiving the washings in a small tared beaker. The filter and casein are dried at 100° for an hour and weighed.

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* Chem. News, 1891—1—56.

† Journ. Amer. Chem. Socy. 1899—980.

Koenig states that in 302 samples of butter the casein ranged from .19 to 4.78 per cent.

Salt. The washings in the beaker are evaporated to dryness in the water-bath and weighed as salt plus milk sugar. The residue is dissolved in hot water, filtered if not quite clear, acidified by a few drops of nitric acid, and the chlorine precipitated by silver nitrate. From the weight of silver chloride is calculated that of the salt.

Another plan is to boil a portion of the butter with water and filter from the fat and casein. The filtrate is titrated by silver nitrate with potassium chromate as indicator.

In 113 butters the percentage of salt ranged from .4 to 9.2, the majority within 2 to 7 per cent.

Sugar. The weight of the sugar is found by subtracting the weight of the salt from that of the salt plus sugar. If a more accurate determination is desired, a large weight of butter is boiled with water, and the aqueous solution filtrated from the fat and tested by Fehlings solution or other method.

Adulterations. In America the principal adulterant or substitute for butter is margarine, less frequently lard. The detection of small quantities of margarine is a matter of some difficulty, though when it forms the whole or the greater part of a mixture, as in commercial butterine, less trouble is experienced. No single one of the following tests can be relied on to establish the fact of adulteration, since it is not difficult to prepare mixtures that will approximate any one constant of pure butter.

Oleomargarine or margarine is a commercial product made by depriving beef or other fat of a part of its stearin. The composition of commercial margarine is stated by Blyth as follows.

Water	12.01
Palmitin	18.31
Stearin	33.50
Olein	24.95
Other fats	.26
Casein	.74
Salts	5.23

The so-called "renovated" butter is made by melting the stale article, drawing off the water containing most of the butyric acid and other offensive products, and separating the curd, then chilling the fat by ice, or rechurning.

The various tests for purity are briefly noticed below. It would appear that many of these could be made quantitative by applying the formula for mixtures (page 16), but from the wide variation from the average for any one constant, both in the butter and adulterant, the results are but approximate at best, and often unworthy of confidence.

1. As a rule, genuine butter when carefully melted yields a practically clear fat, while straight oleos and badly adulterated samples appear turbid.*

2. The *refractive index* of butter-fat at 25° is 1.459 to 1.462, that of margarine is 1.465 to 1.470. Either the Zeiss or Amagat-Jean refractometer is suited for the observation; on the latter instrument butter shows —29 to —31; margarine, —13 to —18; lard, —8 to —14; cottonseed oil, 17 to 23.

3. The unequal solubility in gasoline, absolute alcohol, toluene, phenol, amyl alcohol, etc., has been proposed as a means of distinguishing butter from other

* Analyst, 1892—100.

fats, and is suited for dividing butters from margarines. But the behavior of a mixture of fats can but rarely be predicted from the solubilities of the several constituents.

Valenta's test of the temperature of saturation has come into some use. A mixture of equal volumes of melted fat and glacial acetic acid is heated until clear, then allowed to cool spontaneously while stirring with a thermometer. The temperature of incipient turbidity ranges for margarine from 95° to 100°, while for butter there is a wider variation, generally stated to be between 58° and 68°.

Jean prefers to mix equal volumes of the butter-fat and acid in a graduated tube and read the volume of the upper layer which is the excess of acid over that required for solution of the fat.

Crismer modifies Valenta's test, sealing up the fat with a slightly greater volume of alcohol in a narrow tube and heating until the plane of separation of the liquids becomes flattened. Then the tube is slowly cooled with constant agitation until a marked turbidity appears; this temperature he calls "the critical temperature of dissolution". For genuine butter the average is 100°, for margarine 125°, for cotton oil 116°.*

4. Most animal fats have a *Koettstorfer number* of about 197, while that of butter is higher, from 220 to 233. The determination is made in the usual way — heating a weighed quantity of the sample with a measured volume, an excess, of potassium hydrate in alcohol, then titrating back by standard acid and calculating the reacting alkali. An approximation to the percentage of butter in a mixture may be derived from the formula on page 16, assuming a to be 227, and b, 196.

Heated with a solution of a caustic alkali in alcohol, in quantity insufficient for complete saponification, gives rise to an an ester commonly known as butyric ether — $H(O.C_4H_7O)$ (butyric acid) $+ C_2H_5OH$ (alcohol) $= C_2H_5.C_4H_7O.O$ (ethyl butyrate) $+ H_2O$. The fragrant odor of this compound distinguishes butter from other fats free from butyrin.

After saponification the fatty acids may be combined with barium, the barium determined by converting it into the sulfate and weighing, and the combining proportion of barium calculated.

Following the determination of the saponification equivalent, the neutral solution may be made slightly alkaline and evaporated for a further examination of the fatty acids as below.

5. *Insoluble fatty acids.* The mixed fatty acids derived from most animal and vegetable fats are practically wholly insoluble in water, while of those derived from butter, containing around 8.5 per cent of butyrin and allied fats, a part is soluble in water. We may therefore distinguish butter by the lower proportion of insoluble acids or by its containing soluble acids. In genuine butter the proportion of insoluble fatty acids (the Hehner number) is from 86.5 to 89.5 with a mean of about 87.5. In most other fats the proportion is higher, from 95 to 96 per cent. Hence if a sample shows above 90 per cent, adulteration is very probable, and over 88 per cent is suspicious. Roughly $X = 100 \frac{d-b}{a-b}$ where X is the percentage of foreign fat in a sample of butter; a is 95.5; b is 87.5, and d is the percentage of insoluble fatty acids found on analysis.

A weighed quantity of the butter fat is saponified, the alcohol removed by evaporation, and the soap dissolved in water. From this point the test may

* Blyth, Foods, 350.

be carried out in several ways; the simplest is by acidulation, filtration of the insoluble fatty acids, drying and weighing, either with or without a purification by solution in alcohol and filtration.

Leonard* finds that there is a definite relation between the percentage of insoluble fatty acids and their specific gravity, expressed by the formula $Y = K(1 - X)$, where Y is the percentage; X, the specific gravity; and K a constant $= 951 \pm 1.6$.

6. *Volatile fatty acids.* The fatty acids volatile in steam comprise practically those soluble in water. The Reichert-Meissl Number is the volume in cubic centimeters of decinormal alkali required to saturate the volatile fatty acids from five grams of butter-fat. It is a somewhat variable constant in genuine butter, differences arising from the food of the cow, period of lactation, season of the year, etc. The extreme range may be put down as from 20 to 33; as a rule, however, the number will lie between 23 and 29. The average may be taken as about 27. The values of other fats likely to be used as adulterants are margarine from .5 to 1; lard, 1 or less; cottonseed oil, 1 to 2.

While admittedly imperfect, the fact that the number is derived from a distinguishing property of butter, one impossible to counterfeit by admixtures of the common butter adulterants and only to be imitated by fats not easily procured or unsuitable for other reasons, explains the esteem in which it is held among food chemists. Its weakest point is, of course, the considerable range of the values for genuine butter.

In the original process of Reichert, 2.5 grams of the filtered fat was to be mixed with one gram of potassium hydrate and 20 Cc. of alcohol of 89 per cent. After complete saponification water was added, the alcohol boiled off, then acidified by sulfuric acid to liberate the fatty acids. Fifty Cc. was distilled, filtered, and titrated by decinormal sodium hydrate and litmus. Meissl modified the above by doubling the quantity of fat operated on, hence the original numbers are only about one-half as great as Meissl's.

Wollny† criticizes the directions of Reichert and alleges several inherent sources of error, namely the absorption of carbon dioxide by the alkali and its transference to the distillate; formation of butyric ethers; mechanical carrying over of insoluble acids; retention of volatile acids by the insoluble acids; and variations in the size and shape of distilling vessels and rapidity of distillation. He proposes to reduce the errors by certain modifications of the details.

To prevent losses through etherification, a very concentrated aqueous solution of potassium hydrate may be substituted for the usual alcoholic lye. Henriques' process of cold saponification (page 458) is said to give slightly higher results than the ordinary mode, for the reason that in this case there are formed no ethers of the volatile fatty acids.

Obviously, in one distillation the volatile acids are not wholly carried over into the receiver, as much as 25 per cent of the total being left in the flask. Hence the necessity of following the details of the method regarding the ratio of the volume of the distillate to that originally in the flask. Waller modifies the usual mode of distillation by first collecting 50 Cc. and titrating, then adding 50 Cc. of water to the flask and again distilling 50 Cc. and titrating; and proceeding in this manner until the distillate is practically neutral.

Planchon saponifies the butter-fat as usual by a measured volume of standard sodium hydrate, then adds a volume of standard sulfuric acid exactly equivalent to the alkali — this found by a previous experiment. The solution now contains only sodium sulfate, glycerol, and soluble free fatty acids, the insol-

* Analyst, 1898—282.

† Chem. News, 1889—1—20.

uble fatty acids floating on the surface of the liquid. The insoluble acids are removed by filtration and may be determined by weighing or otherwise; the filtrate is titrated by standard alkali.

Uniting the weight of the soluble fatty acids calculated as butyric to that of the insoluble acids should give a sum of not less than 94 per cent of the weight of the fat.

7. The *Iodine Number* of butter-fat lies between 26 and 40, an average of 56 samples showing 33.32. The Number for lard is from 55 to 65; for cotton oil from 100 to 115; and for margarine from 62 to 75; all showing variations within a wide range.

8. The *heat of combustion* of butter fat is about 9.3 calories; oleo from 9.57 to 9.79; and lard about 9.60.*

9. *Viscosity*. The viscosity of margarine is greater than that of butter fat. Killing observes the viscosity at 40° Cent. against that of water at 20° taken for a standard as 100. The result is the "viscosity number" or "viscosity ratio." Wunder determines the viscosity of a solution of given concentration in chloroform at 20° Cent., under which conditions the value of butter-fat is 344.3, that of margarine 373.2.

10. The *specific gravity* of butter-fat is higher than those of the majority of other fats. For several reasons it is best observed at a temperature of about 35°, compared with water at the same temperature or at 15°. At 37.8/37.8° the gravity ranges from .910 to .914, rarely falling below the first figure; at the same temperature oleo is from .901 to .906; beef fat averages about .904, and lard .905. At 100/100°, butter-fat registers .867 to .870; oleo, from .858 to .863. But some possible adulterants have as high a gravity as butter-fat or higher.

Casamajor proposed that a mixture of alcohol and water be prepared of such a strength that at 15° Cent., drops of the fat neither sink nor float therein; then the gravity of the spirit is ascertained. He states that for butter-fat the gravity should be .926, and for oleo, .915.

11. Under the *microscope* the absence of crystals, and with polarized light an uncolored field, is indicative of pure fresh butter; the appearance is well shown in a photo-micrograph. When crystallized from amyl alcohol and magnified 100 diameters, pure butter-fat shows large disks with acicular edges; margarine shows smaller disks with smooth edges. But mixtures, especially if butter largely predominates, do not always give conclusive appearances.

A photo-micrograph of a slide of butter between crossed Nicols shows only a dull amorphous patch, while one of margarine has a distinctive semi-crystalline appearance.

Opinions differ as to the value of a microscopic examination for proof of adulteration, many believing that the only sure conclusion that can be drawn is that the fat under test has (margarine, lard) or has not (butter) undergone fusion.

12. *Cryoscopic test*. The molecular weight of butter-fat as determined by the method of Raoult is stated at from 696 to 716 as determined in benzene solution — Blyth makes it much lower, about 580, in paraxylene solution — while margarine is from 780 to 883. Determinations are made in a special apparatus, first observing the congealing point of a given volume of the solvent, then the congealing point of the same volume in which has been dissolved a known weight of butter-fat. The molecular weight M is calculated by the equation $M = \frac{P.K}{t}$ where P is the

* Journ. Amer. Chem. Socy. 1896—174.

percentage of butter in the solvent; t, the depression in temperature (the difference in the two experiments); and K, a constant for the special solvent used.

13. Substitutes for the natural *coloring matter* of butter are extensively sold under various fanciful trade-names. The bases of the most common are anatto, curcumine, and oil-yellow. Used in such small quantities, the isolation of the chromogen is somewhat difficult, but can usually be done by extraction with a suitable organic solvent, or better by a mixture of two or more. Or the color may be withdrawn into an absorbent solid, such as Fullers earth, with subsequent extraction by a proper solvent.*

* Journ. Amer. Chem. Socy. 1898—112; Wiley Agric. Chem. Anal. 2—522.

URINALYSIS.

Normal human urine is a clear or nearly clear liquid of an amber color, peculiar aromatic odor, and, except shortly after meals, an acid reaction. It is essentially an aqueous solution of urea, sodium chloride, and earthy phosphates and sulfates, and small amounts of a great number of organic and inorganic bodies. The average composition is in grams per liter.*

Total solids	45.0 to 65.0	Sulfur trioxide	1.5 to 3.0
Urea	20.0 to 50.0	Potassium oxide	2.5 to 3.5
Uric acid	.3 to .8	Sodium oxide	4.0 to 6.0
Creatinin	.4 to 1.3	Ammonia	.5 to .8
Hippuric acid	.4 to 1.0	Calcium oxide	.2 to .4
Chlorine	5.0 to 10.0	Magnesium oxide	.3 to .5
Phosphorus pentoxide	2.0 to 3.5	Iron	.001 to .010

Sulfur dioxide in ethereal sulfates	.090 to .500
Oxalic acid	.020 to .030
Glycero-phosphoric acid	.010 to .020
Propionic, valeric, caproic, and butyric acids	.008 to .080
Indoxyl-sulfuric acid (calculated as indigo)	.005 to .019
Thiocyanic acid	.001 to .008
Paraoxyphenylacetic, paraoxyphenylpropionic, dioxyphenylacetic and paraoxyphenylglycollic acids	.010 to .080
Silicic acid, carbonic acid, hydrogen peroxide, nitrates, nitrites, and metals, *e. g.*, manganese and copper	traces
Xanthin, sarcin, etc	.001 to .010
Phenol, cresol, etc	.005 to .020
Bile salts	.000 to .010
Urobilin, urochrome, etc	.080 to .140
Carbohydrates	.014 to .075
Sarco-lactic, succinic, glycuronic, and oxaluric acids, acetone, inosite, cystin, taurin, urorubinogen, urorubin, pigment of Giacosa, skatoxylsulfuric acid (often in considerable amount), skatoxylglycuronic acid; nephrozymase, pepsin, and other ferments; pseudo-xanthin, para-xanthin, hetero-xanthin, guanin, adenin, etc.; pyrocatechin, quinol, protocatechuic acid, etc	traces
Carbon dioxide (cubic centimeters per liter of urine)	15.957
Oxygen "	.658
Nitrogen "	7.775

The habits of life exercise an influence on the composition of the urine, and marked temporary changes may follow bodily or mental fatigue, excesses, the use of certain articles of food, stimulants, etc. Diseases, especially febrile, tend to raise or lower the percentage of some constituents, and certain grave lesions of the urinary system introduce notable quantities of decomposition products normally absent or present only in insignificant amounts. A test of the urine may give the first warning of an incipient ailment and be of the highest importance in the diagnosis, and in the prognosis as well by increase or diminution as the disease runs its course.

For pathological purposes, only a few of the constituents need be determined. Generally a urinoscopic examination is limited to the total solid contents and a search for albumen and sugar, perhaps urea and uric acid also, except where a specific disease is suspected that is manifested by other than these.

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* Platt, Journ. Amer. Chem. Socy. 1897—382.

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1. *Color.** The coloring matters of human urine are principally the compounds known as urobilin, a dark-brown resinous body, $C_{32}H_{40}N_4O_7$, and uroxanthin or indican; other pigments are uroerythrin, uroglaucin, uromelanin, urophaein, urrhodin, etc. In health the color ranges from light to full yellow, while in certain diseases the urine may be on the one hand almost colorless, and on the other nearly opaque brown. Vogel's scale comprises nine shades ranging from No. 1, pale yellow, to No. 9, brownish-black.

Smith adopts a scale of 50 colors corresponding to standard solutions of iodine in water. Into a medium-sized test-tube is measured five Cc. of the urine to be examined, and into another of equal diameter, five Cc. of an aqueous solution of potassium iodide. Into the latter is run from a graduated pipette a .01 per cent solution of potassium permanganate acidified by sulfuric acid, until the color matches that of the urine. Iodine is liberated from the iodide according to the equation $10KI + K_2Mn_2O_8 + 8H_2SO_4 = 5I_2 + 6K_2SO_4 + 2MnSO_4 + 8H_2O$.

2. Healthy urine is nearly or quite transparent, although on standing for some hours a haze of mucus appears. Turbidity in urine may be due to suspended matter of one or more of the following varieties: uric acid, urates, calcium oxalate, earthy phosphates, calcium carbonate, calcium sulfate, leucin and tyrosin, cystin, mucus, pus, ephithelium, blood, tube casts, spermatozoids, fungi, infusoria, elements of morbid growth, urocyanogen, and entozoa. Cloudiness is frequently due to an alkaline reaction of the urine causing a separation of earthy phosphates, the urine clearing up on acidification.

Cloudy urine is examined by filling a heavy test tube and whirling in a centrifuge until the suspended matter has collected at the bottom of the tube. The clear liquid may then be poured off and the deposit inspected under the microscope with an objective of moderate power. If the nature of the deposit cannot be readily recognized, various solvents and staining materials may assist.

3. The *specific gravity* of normal urine ranges from 1015 (water at 1000) to 1025, averaging about 1019. In disease it may fall as low as 1002 or rise as high as 1040 or more. The determination is made by a Westphal balance or picnometer; or with sufficient accuracy for clinical purposes, by the urinometer, a small hydrometer graduated in specific gravities between the limits found in urine.

4. *Total solids.* Five or ten cubic centimeters of urine is evaporated in a small platinum capsule on the water-bath and the residue weighed. Since urea is in part decomposed into ammonia and carbon dioxide during the evaporation, the dish is inclosed in such a way that the steam passes through a measured quantity of a standard acid; the ammonia absorbed is determined by titration by standard alkali, and calculated back to urea.

A more accurate determination of total solids is by evaporating five Cc. of the urine at ordinary temperatures over sulfuric acid in vacuo.

By multiplying the specific gravity less 1000 by 2.33 (Haesser's number) the product will be nearly the weight of total solids in 1000 parts of urine; it is claimed, however, that the formula fails for certain morbid urines.

5. The *inorganic solids* or *ash* is left on carefully burning the residue from the above determination. To avoid fusion of the chlorides the heat is kept as low as possible, and a safer plan is to lixiviate the char (page 105). Wanklyn remarks that a certain normal ratio, about 1 to 1.65, holds between the inorganic and organic constituents of healthy urine.

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* Tyson, Guide to the Pract. Exam. of Urine, Frontispiece.

6. *Inorganic bases. Calcium* is precipitated by ammonium oxalate from the urine made slightly acid by acetic acid. Notwithstanding the acid reaction, the precipitate of calcium oxalate is always impurified by small amounts of coprecipitated bodies, and is best determined by dissolving, after well washing, in dilute sulfuric acid, and titrating hot by standard permanganate.

The *magnesium* in the filtrate from the above is thrown down by ammonium phosphate and ammonia, and the precipitate calcined to pyrophosphate.

Potassium and *sodium*. The urine is freed from phosphoric acid, the earths, and sulfuric acid by precipitation by a slight excess of barium hydroxide. One-half of the filtrate is evaporated to dryness and ignited gently to destroy organic matter, the residue taken up by ammonium carbonate dissolved in dilute ammonia, filtered, and the filtrate acidified by hydrochloric acid. The solution of the alkali chlorides is evaporated to dryness, ignited gently to drive off ammonium chloride, and weighed. The alkalies may now be separated by platinic chloride (page 387).

The *ammonia* and its compounds come for the most part from the decomposition of urea. If the urine shows an alkaline reaction the free ammonia may be titrated directly by weak standard sulfuric acid, with litmus paper as an indicator. The total ammonia is then determined in the same liquid by boiling with a measured volume of standard potassium hydrate in large excess, until all the freed ammonia is dissipated. The residual alkali is then titrated back by standard acid; the loss in alkalinity equals the combined and free ammonia of the urine. Urea is decomposed by the alkali—$CO(NH_2)_2 + 2KOH = K_2CO_3 + 2NH_3$—but without affecting the result of the determination, for the reason that potassium carbonate has an equal alkalinity with the hydrate when using an indicator not affected by carbon dioxide.

Or all the ammonia may be directly precipitated from the urine by platinic chloride, hydrochloric acid and alcohol, and the (impure) precipitate of ammonic platinic chloride distilled with sodium hydrate; the ammonia is passed into standard acid and determined by a residual titration.

Schloessing's method, though tedious, is free from certain objectionable features of others. The urine is mixed with slaked lime in a shallow dish which is then placed under a bell-jar in close proximity to a dish containing a measured volume of standard sulfuric acid. The ammonia liberated by the calcium hydrate is absorbed by the acid, the operation requiring two or three days for completion. The remaining free sulfuric acid is found by titration by alkali.

Moerner and Sjoquist* remove the phosphates, sulfates, etc., from five Cc. of the urine by barium chloride containing barium hydrate dissolved in a large volume of alcohol and ether. After standing for some hours in a closed flask the liquid is filtered and the filtrate distilled, finally with the addition of magnesia and water. The ammonia (set free by barium hydrate) in the distillate is determined as usual. The residue from the distillation is used for the determination of urea.

The examination of urine for heavy metals such as *lead*, *mercury*, *arsenic*, *antimony*, etc., administered as medicine or otherwise ingested, is done by the usual methods for small amounts in presence of organic matter. The organic constituents can be destroyed by any of the strong oxidizers, perhaps easiest by hydrochloric acid and potassium chlorate. Electrolytic precipitation is suitable for some metals, but Frankel† calls attention to the fact that lead

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* Zeits. Anal. 30—385.

† Chem. News, 1898—2—5.

after passing through the system is in a combination that resists direct electrolytic decomposition.

7. The *acid radicals* in quantity are chlorine, phosphoric and sulfuric. Free acid, mainly phosphoric with perhaps some uric or lactic, may be directly titrated by decinormal alkali or alkali carbonate in a large volume of urine. Should the urine be dark colored, litmus paper is used to show the end-point.

Oxalic acid. A large volume of urine is made ammonical, then distinctly acid by acetic acid. On addition of calcium chloride there falls calcium oxalate accompanied by some uric acid. The precipitate is filtered and treated with dilute hydrochloric acid which dissolves the calcium oxalate but leaves the uric acid. The oxalate is precipitated by ammonia and ammonium oxalate and either ignited and weighed as calcium oxide, or the oxalic radical determined by decomposing the precipitate by sulfuric acid and titrating by potassium permanganate.

Salkowski* evaporates 200 to 500 Cc. of urine to one-third, acidifies by hydrochloric acid, and extracts the oxalic acid by several treatments with ether-alcohol. The extract is filtered and evaporated to dryness; the residue is dissolved in water, evaporated somewhat, and filtered from certain bodies soluble in ether but insoluble in water. Finally the oxalic acid is precipitated by calcium chloride in a faintly acid (acetic) solution, and the precipitate dealt with as above.

Chlorine is determined gravimetrically or volumetrically by precipitation with silver nitrate. The silver chloride is always impure when directly thrown out of urine, and a previous oxidation of the organic matter is always advisable.

For the volumetric determination Mohr recommends to evaporate the urine with ammonium nitrate, heat the residue to low redness, dissolve in water, and acidify by acetic acid, then neutralize by calcium carbonate. The titration by silver nitrate may then be proceeded with, using potassium chromate as an indicator. Pibram prefers to oxidize the organic matter by boiling with potassium permanganate, filtering off the precipitate of manganic hydrate formed.

Instead of the potassium chromate indicator, there may be substituted a drop of red ferric sulfocyanide made by mixing solutions of ferric sulfate and potassium sulfocyanide, this reacting with silver nitrate to form insoluble silver sulfocyanide; bleaching and turbidity give a double indication of the end-point. Volhard would add an excess of silver nitrate in known weight, make up to a definite volume with water, draw off an aliquot part of the supernatant liquid, and titrate by ammonium sulfocyanide with ferric chloride as indicator.

Liebig proposed to titrate the neutralized urine by mercuric nitrate, the reaction with sodium chloride being an interchange of radicals giving mercuric chloride and sodium nitrate, the solution remaining clear. The end-point is shown by a clouding due to a reaction between mercuric nitrate and the urea of the urine, this taking place only after all the chlorine has combined with mercury (page 500). Ostwald explains the reaction by pointing out that as long as there are chlorine ions present to form non-ionized mercuric chloride, no precipitation takes place.

The greater part of the *phosphoric acid* in urine is combined as phosphates of the earths and alkalies, but there is also a small amount of glycero-phosphoric acid.

Total phosphoric acid is determined by first destroying the organic matter by

* Analyst, 1899—249.

boiling the urine with nitric acid or evaporating with sulfuric acid, which treatment also decomposes the glycero-phosphoric acid that may be contained. On now adding ammonia and magnesia mixture there falls ammonium magnesium phosphate, somewhat impure however. The precipitate is dissolved in acetic acid, and the phosphoric acid determined in one of two ways: one the direct titration by standard uranium acetate with potassium ferrocyanide as indicator (page 385); the other by precipitation with uranic acid as ammonium uranium phosphate, which is filtered, washed with a hot solution of ammonium chloride, and dissolved in dilute sulfuric acid. The uranic oxide is reduced to uranous oxide by metallic zinc, and the latter compound reoxidized by titration by standard permanganate. The phosphoric acid is calculated from the permanganate required for oxidation.

The phosphoric acid combined with the earths and alkalies is determined by treating the urine with magnesium chloride solution containing ammonium chloride and free ammonia; the impure magnesium ammonium phosphate is filtered off, dissolved in acid, and the solution titrated as above. The phosphoric acid in organic combinations remains in the original solution, and is found by difference.

Sulfur exists in urine in several forms, mainly combined as sulfates of the inorganic bases, but partly also in ester and other organic combinations.

A. The total sulfur of the urine is found by evaporating a measured quantity with sodium carbonate and nitrate, fusing the residue, lixiviating with water, acidifying by hydrochloric acid, and precipitating the sulfuric radical by barium chloride as usual. Another plan is to destroy the organic matter of the urine by boiling with hydrochloric acid and potassium chlorate until colorless, precipitate by barium chloride, and wash the barium sulfate with water and a hot five per cent solution of ammonic chloride.

B. To determine the inorganic sulfates the urine is acidified by hydrochloric acid and directly precipitated by barium chloride, and the barium sulfate purified and weighed.

C. The difference between the quantities of sulfur found in A and B is the sulfur combined as organic compounds.

Organic constituents.

8. *Oxidizable substances other than urea.* As stated by Smith, there is a definite ratio between the weights of potassium permanganate reduced by cold and boiling urine, in healthy urine about 1 to 3.5, which may rise to 1 to 12 in diabetic urine. His process is to dilute the urine with four parts of water and add it to five Cc. of dilute sulfuric acid containing .001 gram of permanganate. The addition is continued to decolorization. The above is repeated with the diluted urine at a temperature of nearly 100°.

9. *Uric acid.* This is a white crystalline powder of specific gravity 1.86, and has the formula $C_5H_4N_4O_6$. It is nearly insoluble in water and dilute hydrochloric acid, and easily fermented with the formation of ammonium carbonate and other bodies. In urine it is usually combined with sodium or ammonium as urates, sometimes in part free.

An old but inaccurate method depends on the insolubility of uric acid in dilute hydrochloric acid. Urates are decomposed by hydrochloric acid, *e.g.*, $Na_2C_5H_2N_4O_3 + 2HCl = 2NaCl + H_2C_5H_2N_4O_6$. The urine is acidified and allowed to stand for some days, the uric acid slowly separating as a crystalline powder that may be dried and weighed. A more satisfactory plan is to evaporate the urine to dryness, dissolve out urea, etc., from the residue by dilute hydrochloric acid and

alcohol, and submit the residual impure uric acid to decomposition by sodium hypobromite, measuring the nitrogen evolved (page 246).

Insoluble ammonium biurate is formed when urine is saturated with ammonium chloride. The precipitate is filtered and washed with a saturated solution of ammonium chloride, and may be treated in several ways to determine the acid present. The simplest is that of decomposition by hydrochloric acid, drying and weighing the residue of uric acid; or it may be suspended in water and titrated by a standard solution of the organic base piperidine with phenolphthalein. The titrand is standardized against hydrochloric acid; one molecule of uric acid combines with one molecule of piperidine.

Uric acid in sulfuric acid solution is oxidized by potassium permanganate. The first appearance of a faint pink color, permanent for a few moments, is regarded as the end-point. The precipitate of ammonium biurate may be dissolved in a solution of sodium carbonate or simply suspended in water, strongly acidified by sulfuric acid, then at once titrated by N/20 permanganate, of which one cubic centimeter oxidizes .00375 gram of uric acid. An objection to these methods is the difficulty of filtering the gelatinous ammonium biurate.

Argentic urate and argentic magnesium urate are both practically insoluble in water, ammonia and acetic acid, but readily soluble in nitric acid. Haycraft precipitates the uric acid from urine by silver nitrate with the addition of a little ammonia and sodium bicarbonate. The precipitate is dissolved in nitric acid and the silver titrated by ammonium sulfocyanide. Deroide avers that the compound of silver and uric acid is of constant composition, and that if xanthic bodies are eliminated, this process is the most accurate of any known.

In several proposed methods the acid is precipitated as silver magnesium urate by silver nitrate in conjunction with magnesia mixture. Chapek measures the standard silver nitrate solution added, dilutes the liquid to a definite volume, and determines the excess of silver in an aliquot part of the filtrate by standard sodium hydrogen sulfide; the chlorine of the urine does not interfere since silver chloride is soluble in the ammonia of the magnesia mixture. Bartley,* after the addition of magnesia mixture and ammonia, titrates directly by N/50 silver nitrate, finding the end-point by filtering a few drops and testing with sodium sulfide. Ludwig decomposes the precipitate by sodium sulfide, then filters off the silver sulfide, concentrates the filtrate and decomposes by hydrochloric acid; the residual uric acid is filtered off and washed by carbon disulfide to remove sulfur, dried and weighed. Cammerer determines the nitrogen in the precipitate by the method of Kjeldahl and calculates the uric acid therefrom.

Rudisch and Boroschek † object on several accounts to the use of ammonia in the precipitation of magnesium silver urate. They prefer to employ a solution of silver chloride in an aqueous solution of sodium sulfite, and to make the urine strongly alkaline by sodium carbonate. The precipitate is $AgC_5H_3N_4O_3$.

Various other bases have been proposed as precipitants, but no method yet devised has proved entirely satisfactory.‡

10. *Urea* or carbamide is the chief form in which the nitrogen of food is eliminated from the system. An average of about 30 grams is daily excreted by an adult; a continuous excess points to abnormal tissue waste, while a de-

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* Bartley's Medical Chemistry, 641.

† Journ. Amer. Chem. Socy. 1902—562.

‡ Journ. Amer. Chem. Socy. 1897—235.

ficiency indicates diminished metabolism or retention from enfeebling or chronic diseases.

Urea has the formula $CO(NH_2)_2$ and is the type or nucleus of a series of allied bodies formed by replacement of one or both of the amidogen groups by organic radicals. It crystallizes in long prisms colorless and odorless. Boiled with water it is partially transposed to its isomer ammonium cyanate, and when heated to 160° is converted to biuret. Heated with potassium hydrate it is entirely converted to carbon dioxide and ammonia, and with potash and potassium permanganate it is decomposed, but yields no ammonia if perfectly pure (Wanklyn). It is decomposed to nitrogen, carbon dioxide and water by nitric acid containing nitrous acid. In urine it is associated with a ferment (*Torula ureae*) that by assimilation of water speedily converts it into ammonium carbonate.

Basic in character, salts are formed with the stronger acids. The solutions are not precipitated by tannin, lead acetate, or other precipitants of the alkaloids, nor do they reduce Fehlings solution.

Bunsen's method. The principle is that of decomposing the urea by heating the urine with barium hydrate, — the carbonic acid formed being fixed by barium — $CO(NH_2)_2 + Ba(OH)_2 = BaCO_3 + 2NH_3$. In a modification due to Bunge, 30 Cc. of the urine is treated with 10 Cc. of a cold saturated solution of barium chloride containing some free ammonia. After filtering from barium sulfate, carbonate, etc., through a dry paper, 20 Cc. of the filtrate is introduced into a stout glass tube containing 3 grams of solid barium chloride. The tube is sealed and heated to 160° for four hours. The barium carbonate is filtered off, converted to barium sulfate and weighed, and the carbon dioxide calculated. One molecule of carbon dioxide comes from one molecule of urea.

Wanklyn mixes the urine with a strong solution of caustic potash, heats in a retort to 150°, and collects the distillate which contains the free ammonia from the decomposition of the urea — $CO(NH_2)_2 + 2KOH + 2H_2O = 2NH_4OH + K_2CO_3$. The ammonia is determined by Nesslers test (page 376).

Cross and Bevan * find that urea is completely decomposed to nitrogen and carbon dioxide by a mixture of chromic and sulfuric acids containing a little nitric acid. The nitrogen is collected in a gas-measuring tube standing over soda-lye, the alkali absorbing the carbon dioxide. The volume of nitrogen is measured, reduced to normal conditions of temperature and pressure, and its weight calculated. Very accurate results were obtained on pure urea by this process.

By fermentation. Musculus proposes to collect the peculiar ferment of decomposing urine, by passing the urine through filter paper, cutting the paper into strips, and drying at a low temperature, when the entangled ferment remains active for some days. The urine to be tested is neutralized and a few strips of paper introduced. After standing for six hours at about 40° C. in a closed vessel, the free ammonia formed by the decomposition of the urea is titrated by standard acid.

Urine mixed with diastasiferous broth containing urophagous bacilli is also decomposed, though if the urea be above ten per cent the solution is poisonous to the active bacilli. Miguel mixes equal volumes of the broth and urine with enough ammonium carbonate to make the whole slightly alkaline; in a part of the mixture ammonia is at once determined by alkalimetry; another part is heated in a full closed bottle to 50° for two hours and the ammonia determined. The difference is the ammonia from urea.

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* Chem. News, 1889—2—13.

Liebig's method. (1) With mercuric nitrate, urea forms an insoluble white compound — $2CO(NH_2)_2 + 3H_2O + 4Hg(NO_3)_2 = 2CO(NH_2)_2.Hg(NO_3)_2.3HgO + 6HNO_3$. (2) Sodium carbonate precipitates yellow mercuric oxide from mercuric solutions. With these reactions as a basis, urea can be titrated by mercuric nitrate (best standardized against pure urea), the end-point being observed as the yellow precipitate struck with sodium carbonate.

The urine is prepared for the titration by coagulating any albumen by boiling, and precipitating the sulfuric, phosphoric and carbonic acids by baryta water containing barium nitrate. After filtration the urine is neutralized by nitric acid and titrated, the end-point observed by bringing a drop in contact with a paste of sodium bicarbonate and water. The solution must be continuously neutralized during the titration (as by suspended calcium carbonate) or at least at the close, since free nitric acid alters the composition of the precipitate from the normal formula; a correction is to be made for the volume of titrand needed to convert sodium chloride into sodium nitrate. The method calls for many precautions and has largely fallen into disuse.*

Knop's methods. For clinical demonstrations, this method is eminently adapted by reason of its simplicity, rapidity and fair accuracy. The basis is the decomposition suffered by urea when brought in contact with an alkaline solution of a hypobromite, one of the educts being nitrogen; thus, $NH_2.CO.NH_2 + 3NaOBr + 2NaHO = N_2 + Na_2CO_3 + 3H_2O + 3NaBr$. The nitrogen is collected and measured and the urea calculated by the formula of Hufner — $h = \frac{V(b-b')}{760\,(1+.00366t)} \cdot \frac{1}{354.3}$, where h is the weight of urea; b, the height of the barometer, and b' the tension of aqueous vapor at the time of the experiment; $t°$, the temperature, and V, the observed volume of moist nitrogen. The result includes whatever free ammonia may be in the urine. Practically, one gram of urea furnishes 354.3 Cc. of nitrogen.

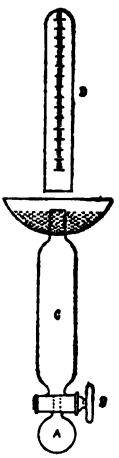

Fig. 184.

But it is well recognized that the full theoretical yield of nitrogen is not obtained under these conditions, since for a given weight of pure urea added to urine, nitrogen corresponding to only about 92 per cent of urea is evolved. In practice the loss is variously stated at from three to ten per cent. Luther explains the discrepancy on the ground that three to four per cent is oxidized to nitric acid, and one to two per cent to a compound yielding ammonia on distillation with sodium hydrate. Fenton ascribes it to the formation of ammonium cyanate. An addition of sucrose or glucose brings the yield nearly up to the theoretical. Allen to prevent the reversion to the isomeric ammonium cyanate, makes an addition of potassium cyanate to the urine before the test; then adds sodium hydrate, finally bromine.

The analysis is made in a glass apparatus, one of the many forms shown in Fig. 184. The lower bulb A holds exactly five cubic centimeters, and is filled with urine up to the stopcock B, which is then closed and the tube C filled with the mixture of bromine and sodium hydrate solution, often referred to as the "bromized soda solution." A gas-measuring tube D is filled with water and inverted over the orifice of C, and B opened. The heavier reagent flows down into the urine in A, and the nitrogen evolved rises into D; when the evolution has ceased D is transferred to a jar of water, and the volume of moist gas read, corrected for temperature and

* Journ. Amer. Chem. Socy. 1901—632.

pressure, and calculated to urea. Under ordinary conditions the volume of the gas is increased by the tension of the aqueous vapor to an extent nearly compensating for the volume of that part of the nitrogen not evolved in the reaction, so that the uncorrected volume may for practical purposes be considered as the absolute volume.

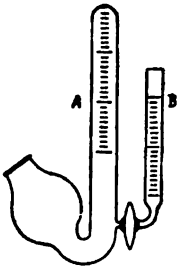

Fig. 185.

The proposal of Davy to substitute a solution of calcium hypochlorite (bleaching powder) or sodium hypochlorite for the hypobromite has the sanction of many chemists.

A simpler though less exact apparatus for the use of physicians is known as the "ureameter" and shown in Fig. 185. It is inverted and the graduated tube A filled with either the bromized solution or one of chlorinated soda. When the apparatus is returned to an upright position the solution is held up by atmospheric pressure. One cubic centimeter of urine is passed into A from B, and the volume of nitrogen rising in A read on the graduations; these show the content of urea directly and save any calculation.

Hamburger, on the assumption that one molecule of urea yields two atoms of nitrogen through the reduction of three molecules of sodium hypobromite, adds to the urine an excess of standard alkaline hypobromite, reduces the excess by standard arsenious acid, then titrates the excess of the latter by iodine solution and starch. The method is pronounced unreliable by Pflueger.

Of other methods that have been published may be mentioned the direct precipitations by oxalic acid, phosphotungstic acid, and orthonitrobenzaldehyd, and the decomposition to nitrogen by Millon's reagent, heating with phosphoric anhydride, etc. It has been proposed to calculate the weight of urea from specific gravity or refractive index determinations before and after decomposition by hypobromite. An approximate clinical determination can be made on the basis of the rise in temperature from the reaction between urea and alkaline sodium hypochlorite.

Nitrogen. From 85 to 90 per cent of the total nitrogen of urine is in the form of urea. The simplest method for total nitrogen is that of Kjeldahl, evaporating the urine with concentrated sulfuric acid, heating until nearly colorless, making alkaline with sodium hydrate and distilling the ammonia, which may be determined in any suitable manner. Caseneuve and Hugouneng prefer to mix the urine with an equal weight of plaster of Paris and a little oxalic acid, dry in an air-bath, mix with oxide of copper, and burn by the method of Dumas (page 304), somewhat modified. When using the soda-lime method, five cubic centimeters of urine may be poured into the filled tube, dispensing with any preliminary evaporation.

Albumen. Absent from healthy urine or exhibited only under temporary lesions of the system, in certain diseases it is a constant symptom, and the detection is therefore an important aid in diagnosis, and the quantity an index to the progress of the disease. For qualitative tests many reagents have been proposed such as uranium acetate, potassium ferrocyanide with acetic acid, picric acid, salicyl-sulfonic acid, mercuric potassium iodide, mercuric succinimid, etc.

The usual test is founded on the property of albumen in solution to coagulate at a moderate heat. The urine is filtered, faintly acidulated by acetic acid to prevent precipitation of earthy phosphates, and boiled for a few minutes. If there be albumen in the urine, a cloud appears, and shortly the albumen separates in flocks if present in considerable quantity.

The albumen may be filtered, washed with alcohol and ether, dried and

weighed. It has been recommended to filter through a plug of purified cotton in a glass filtering-tube by the aid of a vacuum, and wash until no reaction appears with silver nitrate. The tube is dried, first at 100° then at 110° to constant weight, assisting the removal of water by passing dry air through the tube during the desiccation. Should the weight of albumen exceed .2 gram, a second test is made with a smaller volume of urine diluted with water. From the weight is deducted that of the traces of earthy phosphates always left when the albumen is burned.*

The volume of the albumen as deposited after boiling or precipitation may be measured in a graduated tube. In Purdy's modification of Esbach's tube, Fig. 75, the lower portion is drawn to a cone for more accurate measuring. A fixed volume of urine is placed in the tube, the precipitating reagent added, and the tube whirled in a centrifuge until the albumen has compacted in the bottom. The "bulk percentage" is read by the graduations and converted to percentage by weight by a table furnished with the apparatus: over two per cent by weight is unusual. The conditions of time, velocity of the centrifuge, and distance of the end of the tube from the axis of the machine must be the same in all experiments. Esbach's reagent is a mixture of picric acid to coagulate the albumen, with citric acid to hold up phosphates: Purdy's reagent is a mixture of acetic acid and potassium ferricyanide.†

Precipitation by phenol or tannin is the basis of several methods. Van Nuys and Lyons determine the total nitrogen in five Cc. of the urine; then to ten Cc. add an equal volume of tannin in alcoholic solution and some acetic acid, and filter through a dry paper. In one-half of the filtrate is determined the nitrogen; the loss from the preceding determination is the nitrogen of the albumen, and this times 6.24 is the weight of the albumen, including also the globulin. Mehu mixes 100 Cc. of the filtered urine with two Cc. of nitric acid and ten Cc. of a mixture of one part of phenol, one of acetic acid, and two of alcohol. After filtering, the precipitate is washed by a cold four per cent solution of phenol in water, and dried and weighed, or the nitrogen determined by the method of Kjeldahl.

Girgensohn mixes ten Cc. of urine with five Cc. of a 20 per cent solution of sodium chloride, then adds an excess of tannin. After filtration, the precipitate is washed with water to remove salt solution, then with alcohol to remove tannin. The residue is said to be pure albumen.

Potassium ferrocyanide precipitates albumen as a compound containing 211 parts of ferrocyanide to 1612 parts of albumen. Following Boedeker, the urine is mixed with an equal volume of acetic acid and titrated by a standard solution of the ferrocyanide of which one cubic centimeter precipitates ten milligrams of albumen. The indication of complete precipitation of the albumen is the yellow color of the filtrate due to a slight excess of ferrocyanide. The process is tentative, successive trials being made with different ratios of urine to ferrocyanide until with a certain volume of urine a clear yellow filtrate is obtained giving a precipitate with a drop of urine, while the filtrate from a slightly greater volume of urine is nearly colorless and gives no precipitate with urine; the mean of the two volumes is assumed to be the equivalent of the fixed volume of ferrocyanide. For example, ten Cc. of ferrocyanide solution tested 10 Cc. (yellow filtrate) — 20 Cc. (colorless) — 15 Cc. (yellow) — 17.5 Cc. (yellow) — 18 Cc. (colorless) of urine, indicating an equivalent volume of about 17.75 Cc. of urine.

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* Zeits. anal. 27—635.

† Journ. Amer. Medical Assn. 1899—763.

Other reagents that have been proposed for the precipitation of albumen are nitric, metaphosphoric, and trichloracetic acids, mercuric potassium iodide, etc.

The loss in specific gravity and the difference in refractive index before and after precipitation of the albumen by heat furnish approximate tests for urines fairly high in albumen; and for moderate amounts in urine that can be made perfectly clear and is not too dark in color, a polarimetric examination is at once rapid and fairly accurate. Using a 200 Mm. tube, in the Soleil-Ventske polarimeter, each division of left-handed rotation corresponds to one gram of albumen per 100 Cc. nearly.

It is known that the so-called albumen of urine is really but a comprehensive term for an indefinite group of proteids. Attempts have been made with some success to differentiate these but the methods are hardly suitable for technical analysis.

13. *Sugar.* Dextrose in more than traces is an abnormal constituent of urine and an indication of the disease known as diabetes mellitus. Usually diabetic urine is of higher density and paler in color than when normal.

The carbon dioxide evolved on fermentation by yeast may be determined by any of the usual methods, but the process is subject to the uncertainties attending any estimation of sugar in a complex mixture by fermentation unless corrected by a parallel test, and moreover is interfered with by antiseptics that may be in the urine, derived from medicines exhibited or otherwise. To remove interfering bodies Bishop advises to shake up the urine with animal charcoal, and when colorless to add baryta water and boil. After cooling and filtering, copper sulfate is added to the filtrate in moderate excess, and after standing for an hour in a covered vessel is decanted and filtered. The copper is removed from the filtrate by hydrogen sulfide, and the excess of hydrogen sulfide by heating. The liquid is now ready for a determination which may be made in the usual way (page 429).*

A simple apparatus, Fig. 186, was devised by Einhorn for clinical use. The tube A is inverted and filled with urine, then turned upright and a little yeast introduced. The apparatus is kept in a warm place until the evolution of gas ceases, and the volume of carbon dioxide read by the graduations which are spaced to show percentages of sugar directly, allowing for the retention of carbon dioxide in the urine and other factors.

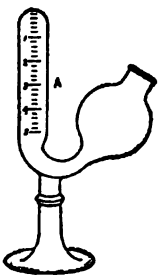

Fig. 186.

The specific gravity of diabetic urine is lowered through fermentation of the saccharine matter, and the reduction is a fair index of the sugar content.

The rotation of the plane of polarized light by dextrose ($+52°$), as observed in the polarimeter, is an easy test, and under certain conditions may be quite as accurate as any other method. However, albumen and some other constituents of urine also rotate the plane. Such interfering constituents can be removed by the usual reagents, but clarification by lead acetate is unsatisfactory for the small quantities of sugar contained in urine, and even for exceptionally high percentages; a better medium is talc powder.

Phenylhydrazin yields a precipitate of glucosazon with the sugar of diabetic urine. Von Jaksch removes any albumen by boiling, filters, adds to the filtrate sodium acetate and phenylhydrazin hydrochloride, and heats the liquid

* Amer. Journ. Pharm. 1898—450.

to 100° for a half hour. If the precipitate falls in an amorphous condition it is filtered off, dissolved in hot alcohol, diluted with water, and the alcohol boiled off, when the precipitate will reappear on cooling as yellow prisms.

As a qualitative reagent this compound has distinct advantages over others but is inferior for quantitative work. Coriat* finds that substances interfering with Fehlings and Nylanders tests do not modify the reaction with phenylhydrazin, nor is it necessary to remove albumen. The limit of delicacy as a qualitative test is said to be one part in 10000 of liquid.

A colorimetric method due to Johnson is that of boiling the urine with addition of picric acid and potassium hydrate which gives with sugar a dark mahogany-red color. For a standard a solution of pure grape sugar is treated in the same manner, or more comparably a normal urine compounded with a weight of grape-sugar approximately equal to that in the urine under examination.

More prominent than any other method is the volumetric determination by titration with Fehlings solution. But certain other constituents of urine interfere somewhat, notably creatinin and uric acid, also xanthin and its analogues that give a precipitate containing a cuprous-xanthin compound instead of pure cuprous oxide. It is said that the reducing power of normal urine is on an average equal to .3 per cent of glucose.

Albumen, if present in the urine is coagulated by acidification and boiling, the filtrate is made alkaline and filtered from phosphates, and xanthin bodies removed by precipitation by copper sulfate. A measured quantity of Fehlings solution is then titrated by the filtrate. Pavys ammoniacal copper solution is to be preferred to the original Fehling since any free ammonia in the urine would dissolve some of the precipitate of cuprous oxide; the titration is conducted under a layer of melted paraffin, the burette tip immersed in the urine. For routine work the solution may be made up of such a strength that one cubic centimeter represents one milligram of dextrose, the sugar solution being approximately of a given concentration.

Knapps mercuric solution (page 488), is preferred by some authorities to that of Fehling or its modifications.

14. *Creatinin.* The method of Liebig † is to exactly neutralize the urine by milk of lime, and add calcium chloride as long as phosphoric acid is precipitated. The filtrate is evaporated to a small bulk, decanted from crystals of sodium chloride, etc, and treated with zinc chloride and left for several days. Creatinin zinc chloride separates in nodules, to be filtered and washed with a little cold water, then with alcohol. The compound is decomposed by lead hydroxide to creatinin, zinc hydrate, and lead chloride, filtered and concentrated, and the creatinin extracted from creatin by absolute alcohol. Johnson regards the creatinin obtained by the above process as having undergone some change, for the reason that its reactions differ somewhat from those given by creatinin extracted without application of heat.

Neubauer separates the phosphoric, sulfuric and carbonic acids of the urine by calcium oxide and chloride, or by barium hydrate and nitrate, evaporates the filtrate to dryness, extracts the residue with alcohol, and precipitates the creatinin by zinc chloride in alcoholic solution. The precipitate has the formula $(C_4H_7N_3O)_2.ZnCl_2$.

Gautrelot and Viellard determine creatinin indirectly, calculating its weight from three determinations of nitrogen — (1) on the original urine; (2) on the filtrate from the urine precipitated by basic lead acetate; and (3), on the fil-

* Journ. Amer. Chem. Socy. 1900—19.

† Allen, Coml. Org. Anal. 3—3—288.

trate from the urine precipitated by lead acetate and zinc chloride. In the first determination is found the total nitrogen of all nitrogenous bodies; in the second, that of creatinin and nitrogenous bodies other than urea; and in the third, that of nitrogenous bodies other than urea and creatinin.

15. *Acetone.* A method due to Engel and Deveto is as follows. From the urine passed during 24 hours is drawn from 30 to 100 Cc. which is diluted with an equal volume of water. A little acetic acid is added to retain phenol, and the liquid distilled to one-tenth. The acetone passes into the distillate, and after qualitatively testing the residue in the retort to insure that all has passed over, the distillate is redistilled with the addition of a little sulfuric acid to retain ammonia. To this distillate is added an excess of decinormal iodine solution and sodium hydrate which react with the acetone —

$$CH_3.CO.CH_3 + 3I_2 + NaOH = CHI_3 + CH_3.COONa + 3NaI + 3H_2O.$$

The excess of iodine is then titrated back by decinormal sodium thiosulfate and the weight of acetone calculated from the above equation.

16. *Xanthin bases.* According to Salkowski these are not true xanthin but more nearly resemble hypoxanthin. He directs to first precipitate the phosphates from a liter of urine by magnesia mixture; then after filtering, the xanthin, uric acid, etc., by ammonium silver nitrate. The precipitate is suspended in water and decomposed by hydrogen sulfide and the filtrate evaporated to dryness. The xanthin is extracted from the residue by weak sulfuric acid, leaving the uric acid; the filtrate is again precipitated as before. The silver in the precipitate is converted to chloride and weighed, and the xanthin calculated. Normal urine is said to contain from .0027 to .0030 gram of xanthin bodies per 100 Cc. of urine.

Krueger and Woolf free the sample of urine from albumen, if present, by boiling. The xanthin bodies are then to be precipitated by a mixture of sodium bisulfite and copper sulfate with a little barium chloride to promote settling; in a few hours the precipitate is filtered and washed with air-free water. The nitrogen in the precipitate is determined by Kjeldahl's process, and the difference between the result and nitrogen previously found to exist as uric acid is the nitrogen of the xanthin and allied bodies.

Hoffmeister removes xanthin from urine by hydrochloric and phosphotungstic acids, the reagents employed by Von Pohl for the precipitation of leucomaines for their quantitative determination.

For the determination of various other normal and abnormal constituents of urine the student is referred to the numerous monographs on the subject.

THE ORGANIC DYE-STUFFS.

The phenomenon of the fixing of a dye-stuff by animal or vegetable fibers is variously interpreted by different writers on the subject. The theories advanced are mechanical or chemical or combinations of the two. The adherents of the mechanical theory "assume that the coloured particles gradually leave the dye-bath to fix themselves between the molecules of the fibre without any chemical action". The chemical theory "presumes that a chemical combination takes place between the fibre and colouring matter, e. g., the salt of a coloured base is dissociated by the fibre", and it is asserted that all the phenomena of dyeing premise two essential conditions — the presence of acid or basic functions in the fiber and also in the coloring matter. The only exceptions are the tetrazo-dyes.*

A number of attempts have been made to classify dye-stuffs according to their chemical composition. That of De Konstanecki is given below,† the dyes arranged according to the nature and number of their chromophores all of which contain double bonds.

A. Coloring matters containing a single chromophore.

C : C.	Diphenylene-ethane.
C : O.	Oxyketones, oxycoumarines, oxyanthones, oxyflavones.
C : N.	Auramine, thioflavine, quinoline yellow.
O : N : O.	Nitro-coloring matters.
N : N.	Azo-colors.
N : N : O.	Azoxy-colors.

B. Coloring matters containing several chromophores.

1. Streptostatic chromophores (ketone type).

C : C with C : O.	Unsaturated oxyketones, indogenides, oxyindogenides, indigo.
C : O with C : O.	Oxydiketones, oxydianthones.
C : N with C : N.	Hydrazone coloring matters.
N : N with N : N.	Diazo colors.

2. Cyclostatic chromophores (quinon type).

C : O with C : C.	Aurines, benzeines, phthaleins.
C : O with C : O.	Oxyquinones.
C : N with C : C.	Basic coloring matters of the triphenylmethane group, pyronines.
C : N with C : O.	Indophenols, nitrosophenols.
C : N with C : N.	Indamines, azines, safranines, indulines.
C : N : O with C : O.	Resazurine.

3. Streptostatic and cyclostatic chromophores.

This group comprises several complicated coloring matters such as alizarin blue, styrogallol, etc.

Natural products of interest to the dyer are indigo, madder, logwood, saffron, barwood, and others of less importance. Their quality varies greatly with the locality of growth, time and manner of collection, age, and care in preservation. They are found in commerce in bulk or powder, or as liquid or solid extracts, the latter, however, offering greater opportunities for successful adulteration.‡

The enormous development in recent years of the manufacture of artificial dyes has resulted in the practical retirement of many of the natural wares formerly held in high esteem, until at present there remain but few that possess more than a historical interest.

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* Journ. Socy. Dyers & Col. 1893—44 and 1897—63.

† *Idem*, 1897—27.

‡ *Idem*, 1892—9.

In determining the value of a commercial article it is to be remembered that from an assay of the leading constituent or constituents there may be drawn conclusions quite unlike those from a test along the lines of the practical employment of the substance, and this rule is eminently true of the natural dye-stuffs, complex bodies whose impurities exercise a great influence on the behavior of the dye-bath; and also in some degree applies to the artificial dyes.

1. The dye-test. The oldest and best known scheme for finding the quality of a dye-ware is a miniature dyeing test made under the same conditions as apply in practice. Opinions differ widely as to the value of this form of assay, some holding that when properly performed the results can be accepted with assurance of confirmation when working on a large scale, while others deny it to be more than a rough approximation, for the reasons that it is impossible to follow closely the practice of the dye house on a small scale, and that in judging the results considerable latitude is to be expected among different observers and at different times by one observer. But conceding that the test often proves neither exact nor reliable in the hands of the inexperienced, it must be allowed that an expert, well acquainted with the dyeing processes employing the ware examined, can deduce reliable estimations as to the quality of a sample.*

Essentially an empirical process modified to conform with the practice of the dye house, no details for the test can be formulated that may be followed without modification. The tests are made on cloth or yarn of clean cotton, wool or silk, mordanted or not to conform to the kind of fiber and nature of the dye. In general a weighed amount of the dye-stuff is brought into solution in a fixed volume of solvent, the prepared fiber digested for a given time and at a given temperature, withdrawn, washed, dried, and the color, shade and luster compared with a standard. It is always advisable to make a parallel test upon another sample of the given dye that has yielded uniformly good results in practice, with all the conditions practically identical. And in comparing two samples it is well to make several trials, diluting the stronger solution until the shades or tints of the dyed hanks are the same, using equal volumes for the baths. The relative strengths of the dyes are then directly proportional to the dilutions.

As an example, Kratz† in testing extract of logwood proceeds in this way. White woolen yarn is washed, dried, and divided into ten-gram hanks. The mordant solutions are for one hank two per cent bichromate with two per cent bisulfite; for two other hanks, two per cent bichromate with two per cent tartar. One of the latter two is then passed through a hot two per cent solution of soda. After mordanting all hanks, they are washed. Exactly eight grams of each dye to be tested is washed into a liter flask with boiling water, stirred well, allowed to cool and made up to the mark. For each sample, three hanks prepared as above are dyed in 100 Cc. of the dye solution, boiling for one hour. The baths are then allowed to cool for a half hour, and the hanks washed. The hank showing the best dye signifies the best extract.

Von Cochenhausen directs to use as mordants (1), a strong oxidizer, as bichromate; (2) one not so strong, as bichromate with tartar; (3) a non-oxidizer, as alum with tartar. It is recognized that the best logwood extract loses its value if an expensive and complicated mordanting process must be adopted.

2. Colorimetric methods can be applied to most dyes. The standards for

* Journ. Socy. Dyers & Col 1896—82.

† *Idem*, 1892—49.

comparison may be either the dye itself or its chromofer in a state of chemical purity, or another compound possessing the same color. Many of the coal-tar dyes come on the market almost chemically pure or can be made so by a simple purification, and are thus fitted as standards for the same or analogous commercial dyes or for vegetable dyes of corresponding colors — thus a 2.5 per cent solution of thioflavin is said to exactly match a .1 per cent solution of curcumine (the basis of turmeric). Some inorganic salts can be used for the same purpose, *e.g.*, potassium bichromate for saffron. And often the standard is a particular sample of the commercial dye-stuff known from its history or by practical use to be of a desirable quality.

For extract of logwood Mafat* compares the diluted extract with pure haematin as a standard; since a common impurity of the commercial extract is a mixture of treacle and chestnut-extract in the ratio of two parts of the former to one of the latter, he prepares a series of ten tubes of 100 cubic centimeters capacity, the first of ten grams of the pure extract; the second of 9.5 grams extract, .33 gram of treacle, and .17 gram of chestnut-extract; the third of 9 grams of extract, .67 gram of treacle, and .33 gram of chestnut-extract; and so on.

The distrust of colorimetric methods for dye-wares that has been expressed in some quarters is not without foundation, for it must be considered that in a solution of a dye of given concentration the depth of color is one thing and the dyeing capacity another, and it will not do to assume that the two are identical or even strictly comparable. Moreover the bodies associated with the chromogen may modify the color, many dyes are more or less dichroistic, and the color of even a largely diluted solution is still so intense that a slight variation in tint is impossible to observe.

Schoop† recommends the spectroscope as a means of quantitative determination for coal tar colors.

3. By a direct determination of the chromogen or an auxichrome or some associated body that bears a definite proportion to it. The most direct and satisfactory method is the isolation of the chromogen in the pure state, but this is seldom practicable. The active principles of some of the vegetable and animal and many of the coal tar dyes are acid or basic in character, or form definite compounds with reagents and so admit of a gravimetric or volumetric determination. For example, all of the basic coal-tar derivatives are precipitated by tannic acid and many by various inorganic salts, notably lead acetate, aluminum sulfate, alum, and barium chloride; the tripheny-methane colors by virtue of the amido- and hydroxyl groups they contain, have the property of taking up one or more atoms of bromine in ortho- or para-position; the phenylated derivatives of rosaniline show a similar behavior; etc.

Some of the coal-tar colors are decolorized by sodium hyposulfite at 100° Cent., and this is made the basis for a volumetric determination; in many cases the end-point is sharp and the titration easy. One method is to measure two equal volumes of the hyposulfite solution into flasks and cover them with layers of kerosene. The two dyes to be compared are dissolved in water to suitable volumes and run in from burettes until the colors show faintly. It is said that one molecule of magenta, Hoffman's violet, Paris violet, etc., requires the same volume of hyposulfite solution for decolorization as do two molecules of ammonium cupric sulfate, affording an easy means of standardization.

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* Journ. Socy. Dyers & Col. 1892—93.

† *Idem*, 1886—71.

Rawson* applies the reaction between night-blue and napthol yellow S (anilin dyes), the two combining to form an insoluble compound in the ratio of two molecules of the former to one of the latter. He proceeds by dissolving ten grams of pure night-blue in glacial acetic acid and diluting to one liter, also one gram of the sample of napthol yellow to be tested in a liter of water. Into ten Cc. of the former is run about 30 Cc. of the latter and the mixture filtered. If the filtrate is blue or yellow, other tests are made, increasing or reducing the volume of the napthol yellow until a proportion is reached where the filtrate is but faintly yellow. Of several samples the dyeing values are inversely as the volumes required.

The decomposition of the chromogen may furnish products that can be determined; thus the yellow chromophyl of saffron is a glucoside yielding on treatment with sulfuric acid, glucose, crocine ($C_{16}H_{18}O$) and an essential oil $C_{10}H_{14}O$; curcurmine, the chromogen of turmeric, yields oxalic acid when treated with nitric acid, and pyrocatechuic acid on fusion with caustic potash.

4. By absorption of the chromogen in a porous solid. Some of the dyes are completely withdrawn from a solution by vegetable or animal fibers and by certain inorganic compounds. The amount absorbed may be determined directly by the increased weight of the fiber or by the diminished weight of the residue left on evaporation of the solution. And generally the dye may be recovered by boiling the fiber with certain solvents.

Thus the coloring matter of logwood (haematoxylin and haematin) resembles tannin in being absorbed by hide powder. A weight of the extract is diluted, an aliquot part evaporated to dryness, and the residue weighed. An equal volume is also evaporated after percolation through a column of purified hide powder. The difference in the weights represents the coloring matter taken up by the hide. Obviously if the extract contained any tannin as a constituent of an adulterant, this would also be absorbed and count as coloring matter.

5. By determination of some associated constituent normally present in the dye-stuff and not contained in the usual adulterants. Some of the extracts of the vegetable dyes and coal-tar colors retain certain matters originally in the crude article or that have been formed in or introduced during the processes of manufacture. A determination of this kind is always open to criticism, and should only be resorted to under exceptional circumstances and never relied on in important cases.

For example, the most common adulterant of saffron is an amido-azo compound known as féminelle, which differs from saffron in containing no crocetine (the coloring matter), and in having a much larger amount (7.44 per cent) of chlorine than has saffron (.23 per cent).†

6. A microscopic examination, besides detecting impurities, may possibly allow a fair estimate to be formed of the proportion of pure dye in a mixture.

Many of the commercial dyes and extracts are sent into the market in the form of a paste or in suspension in water; others dry, in admixture with some cheap inert body. The object of retaining some dyes in moist condition is that evaporation or drying would impair their ready solubility in the dye-bath. The use of 'fillers' is for the purpose of preventing deliquescent colors from setting to a solid mass, to allow the weighing out by workmen of a charge for a dye-bath on ordinary scales, or, the filler being white and in a definite ratio

* Journ. Socy. Dyers & Col. 1888—82

† *Idem*, 1898—236.

to the dye, to lessen the intensity of the color and make easier an estimation of the proper amount to be used. These fillers are commonly salt, sugar, gypsum, sodium sulfate, magnesium sulfate, etc., and are not to be considered as adulterations except where the proportion exceeds that specified at the time of purchase. Usually the proportion is 50, 75, 80 or 90 per cent of the mixture.

The analysis of an extract or dye is about as follows.*

Moisture, carbon dioxide, and *matter insoluble in cold water* are determined by the usual methods for these bodies and need no detailed mention.

In the matter insoluble in cold water or alcohol will be found any *starch* that may be in the dye. Where the remainder of the insoluble matter is wholly inorganic, the loss on ignition of the residue is taken to be the weight of the starch, but if partly organic, the starch is extracted by hot dilute hydrochloric acid and determined by the usual methods.

Sulfates of *calcium, magnesium* and *sodium,* and *sodium chloride.* The bases of these compounds will be found in the ash when a quantity of the sample is burned in a large platinum crucible or dish, and may be separated and determined.

Sulfuric acid, combined with alkalies or earths, is determined by lixiviating the dye with hot dilute hydrochloric acid until no more is extracted, then precipitated by barium chloride. Any adhering barium sulfonate ($Ba(RSO_3)_2$) can be separated by digesting the precipitate with ammonium carbonate solution which reacts with the sulfonate but not with the sulfate. After filtering and washing, the barium carbonate is dissolved from the precipitate by dilute hydrochloric acid, and the barium sulfate weighed.

Chlorine may be combined in the dye itself, or in the form of sodium chloride. If only as the latter the usual course of precipitation as silver chloride is followed, but if in both forms, the sample is first incinerated at a low heat and the sodium chloride extracted from the ash by hot water; then precipitated by silver nitrate. The total chlorine is determined by the conventional methods for this element in organic bodies.

Dextrin and *sugar.* Dextrin may be determined by treating the sample with a little water, then precipitating by addition of alcohol. On filtering and weighing the residue and deducting the weight of the matter insoluble in water, the difference may be set down as dextrin. The result, however, is apt to be too high since other bodies soluble in water may be precipitated by alcohol.

Sugar may be polarized after extracting the dye by absolute alcohol or some other organic solvent in which sugar is insoluble; or the coloring matter may be precipitated from the aqueous solution by basic lead acetate, and the filtrate polarized, then the liquid heated with hydrochloric acid which precipitates the lead and inverts the sugar, and the determination made by Fehlings solution.

Arsenic is determined by fluxing the dye with a mixture of sodium carbonate and nitrate which destroys the organic matter and converts the arsenic to sodium arseniate. The melt is lixiviated with water, and the arsenic precipitated by magnesia mixture and ammonia, and weighed as magnesium pyroarseniate. The precipitate is redissolved and examined for magnesium pyrophosphate that may have been precipitated at the same time.

For various reasons the common adulterants of a given dye-stuff may be restricted to one class of bodies and so be more readily detected and determined than if more varied.

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* Journ. Anal. Appl. Chem. 1892—368.

For example the vegetable extracts are frequently fortified by the cheaper anilin dyes of corresponding color; as cudbear extract by magenta. In this case the orceine (the chromofer of cudbear) can be completely precipitated from a dilute alcoholic solution by basic lead acetate followed by ammonia, magenta remaining entirely in solution. The filtrate may be acidified by acetic acid and compared colorimetrically with standard solutions of magenta acidified by acetic acid. Presumably no other adulterant will accompany the magenta.

ALIZARIN.

Madder is the root of the *Rubia tinctorium*. It contains but little already formed coloring constituents, but in it are several glucosides that yield alizarin (dihydroxy-anthraquinon, $C_{14}H_8O_4$) on fermentation. Alizarin is the essential dyeing principle, and is now made artificially at so low a cost that it bids fair to supplant that derived from madder. When perfectly pure the two alizarins are identical, but the madder-alizarin of commerce always contains purpurin (hydroxy-anthraquinon, $C_{14}H_8O_5$), and the artificial product usually anthraquinon ($C_{14}H_8O_2$) an intermediate product in the manufacture. On moderate heating, the first sublimate from madder-alizarin will be pure alizarin in yellow needles; in that from the artificial variety anthraquinon may be distinguished.

The basis of the manufacture of artificial alizarin is anthracen, obtained very impure as the third fraction of the distillation of coal-tar.* After partial purification it is sent into the market from 40 to 60 per cent pure, containing varying amounts of pyrene, napthalene, crysene, methyl-anthracen, carbazol, etc. Some of these impurities closely resemble anthracen in chemical and physical properties but have less or no value for the purpose intended.

The manufacture of alizarin comprises four stages.

1. On heating anthracen with a strong oxidizer it is converted into anthraquinon — $C_{14}H_{10} + 3O = C_{14}H_8O_2 + H_2O$. For cheapness a mixture of potassium bichromate and sulfuric acid, furnishes the oxygen. The anthraquinon is separated by a centrifugal machine and purified by dissolving in sulfuric acid at 110°; on cooling, part of the anthraquinon separates, the rest on dilution with water. Now about 90 per cent pure, it is in the form of a gray or yellowish powder that may be still further purified by boiling with soda.

2. On heating anthraquinon with concentrated sulfuric acid there are formed three products, their proportion varying with the temperature and time of digestion. If the heat be kept below 160° there is formed anthraquinon-monosulfonic acid $C_6H_4(CO)_2C_6H_3.HSO_3$; from 160° to 170° beta-anthraquinon-disulfonic acid; and if the heat rises to 180° to 185°, alpha-anthraquinon-disulfonic acid; both the latter compounds having the formula $SO_3H.C_6H_3(CO)_2C_6H_3.HSO_3$.

3. The mixture is melted with caustic soda. The anthraquinon-monosulfonic acid yields sodium alizarate — $C_{14}H_7O_2.HSO_3 + 4NaOH = C_{14}H_6O_2(NaO)_2 + Na_2SO_3 + H_2 + 2H_2O$; the reducing action of the nascent hydrogen being prevented by the addition of a little potassium chlorate. The alpha-anthraquinon-sulfonic acid yields principally flava-purpurin, and the beta-acid, anthrapurpurin though some sodium alizarate also — $C_{14}H_8(SO_2)_2O_4 + 6NaOH = C_{14}H_6Na_2O_4 + 2K_2SO_4 + 4H_2O$.

4. On acidifying the lixiviation of the melt there precipitates 'colorin', a

* Journ. Socy. Dyers & Col. 1897—81.

mixture of alizarin ($C_{14}H_6Na_2O_4 + HCl = C_{14}H_8O_4 + 2NaCl$), flavapurpurin, and anthrapurpurin; on the relative proportions of these depends the shade of the dye.

For the assay of commercial anthracen, an old method is that of washing out the impurities by alcohol in which anthracen is insoluble, but the separation is never more than approximate. The method due to Luck, variously modified, is in common use; it is based on the oxidation of the impurities (acenapthen, fluoren, phenthren, carbazol, fluoranthren, etc.) to acids soluble in water, or to their entire decomposition by the action of a strong solution of chromic acid in glacial acetic acid, while anthracen is converted to anthraquinon. It is said that the addition of nitric acid to the reagent gives a more thorough purification and also insures a final product of anthraquinon of a clear yellow color indicating its purity.* After digestion with this powerful oxidizer for several hours and dilution with water, anthraquinon separates in crystals that may be collected, washed with water and weak lye, dried and weighed. Still somewhat impure however, treatment with fuming sulfuric acid sulfonates any remaining impurities, and dilution with water leaves the anthraquinon almost perfectly pure with the exception of some mineral matter that may be deducted after a determination of the ash. Should paraffin be suspected in the sample a preliminary heating with fuming sulfuric acid will leave the paraffin unchanged.

Crude anthraquinon contains, among other impurities, some undecomposed anthracen, and when treated with concentrated sulfuric acid all these are sulfonated, the anthraquinon dissolving unchanged if the temperature be restricted to 130°. On lixiviating the mass with hot water the impurities dissolve, leaving the anthraquinon, still somewhat impure, however. The purification must be restricted, since if carried to complete conversion of the anthracen, certain of the impurities become oxidized to forms not readily soluble in water. The residual anthraquinon is washed and dried, then further purified by fuming sulfuric acid.

The conversion of anthraquinon should be conducted according to the process adopted in the factory — thus for a scarlet shade a larger weight of sulfuric acid and longer heating is required than for a blue shade; in the latter the products are roughly 55 per cent of the monosulfonic acid, 15 per cent of the alpha- and beta-disulfonic acids, and 30 per cent of unattacked anthraquinon; but in the former very little unattacked anthraquinon is left.

After the digestion with sulfuric acid the residue is diluted with hot water and the residual anthraquinon filtered off and analyzed by drying and dissolving in chromic and acetic acids as above; but the subsequent purification by sulfuric acid is unnecessary and omitted.

Should the relative proportions of the two disulfonic acids be desired, the solution is neutralized by sodium carbonate and evaporated until crystallization begins; on cooling, the sodium salt of the alpha-sulfonic acid remains fairly insoluble in water; and on drying, oxidation with nitric acid, and incineration there is left sodium sulfate from which the organic compound may be calculated. The difference is the sodium beta-disulfonate in the filtrate.

Otherwise, the mixture of the acid is heated under pressure at a fixed temperature with concentrated soda-lye containing some potassium chlorate, the latter to prevent any reduction to anthraquinon. At stated intervals during the number of hours required for conversion, samples are withdrawn, dissolved in a measured volume of water, and the alizarin precipitated by acid and

* Chem. News, 1896—1—118.

weighed; a sufficiently close approximation may be had from the apparent volume of the precipitate or the color of the filtrate.

The anthraquinon-monosulfate of sodium found in commerce is generally so pure that only a moisture determination is required.

Alizarin is insoluble in cold, slightly soluble in hot water, insoluble in dilute acids, but readily in concentrated sulfuric. It is found in commerce in the form of a 20 per cent paste of either a blue or yellow shade. The blue shade consists chiefly of alizarin, while the yellow is mainly anthra-purpurin and flava-purpurin (trioxyanthraquinons) with some alizarin.

The quality is often judged by a dyeing test made along with a standard alizarin, about as follows: the cloth is in the form of strips of cotton about ten inches long properly mordanted; the dyeing vats preferably thin glass beakers holding 600 Cc. and heated side by side in a water-bath. Five grams of the dye-paste is suspended in one liter of water, and from this 50 to 70 Cc. withdrawn and added to 500 Cc. of water containing a minute amount of calcium acetate. The temperature is raised to 80°, the strips immersed for an hour, then passed through two soaping baths, dried and examined.

For the valuation of commercial alizarins, there is determined the moisture (at not over 100°) and the ash. A weighed quantity is dissolved in sodium carbonate solution and filtered from the undissolved anthraquinon and oxyanthraquinon — these are separable by caustic alkali or lime. The filtrate is acidified by hydrochloric acid and the precipitate boiled with milk of lime to remove anthraflavic and isoflavic acids. The undissolved lime-lakes are made into a paste with water, decomposed by hydrochloric acid, and the residue — a mixture of alizarin, flavapurpurin and anthrapurpurin — washed and dried.

The separation of the three compounds is difficult. An approximate isolation of the flavapurpurin follows boiling with benzol in which it is soluble. Schunck and Roemer propose a qualitative test by placing a small quantity of the mixture, dried at 100°, on a glass plate on which stands a lead ring a few millimeters high; the ring supports another glass plate. On heating the lower plate to 140°-150° the alizarin volatilizes and escapes; if now the temperature is raised to 170° a sublimate of a mixture of flava-purpurin and anthrapurpurin is obtained. The two are distinguishable under the microscope.

In commercial alizarins any oxyanthraquinons as impurities can be determined by boiling with calcium hydrate and filtering. They communicate a brown color to the filtrate, and on addition of an acid are thrown down. A fair assay of natural alizarin can be made according to Schunck by prolonged sublimation at 140°, this temperature being higher than the point of vaporization of alizarin, but lower than that of the common impurities.

INDIGO.

Commercial indigo is prepared by a peculiar process from the various species of *indigofera*. The plant containing the basis indogen or indoxyl C_8H_7NO, is fermented with water and a little lime, during which indigo is deposited as a powder; this is strained off, dried, and cut into cakes. As sold in the market it is in the form of lumps of a dark blue color, developing a bronze reflection on rubbing with a hard material. As a rule the softer a specimen of indigo the better the quality, but contrary to the opinion of some, the content of indirubin is said to bear no relation to the color.

Indigo is a complex substance, the principal constituents being indigotin or indigo blue $C_{16}H_{10}N_2O_2$ or $C_6H_4\left\{\begin{matrix}CO\\NH\end{matrix}\right\}C:C\left\{\begin{matrix}CO\\NH\end{matrix}\right\}C_6H_4$; indirubin or indigo

red; indiglucin $C_6H_{10}O_6$, a colorless or light yellow sweet compound; indican, $C_{26}H_{31}NO_{17}$, a light brown syrupy glucoside by whose decomposition indigotin, indirubin, and a sugar are formed; and indiretin or indigo brown, $C_{18}H_{17}NO_5$, a dark brown resinous compound.

The composition of commercial indigo varies greatly;* thus:

Indigotin	20 to 80	per cent.
Indirubin	2 to 10	"
Indigo brown	1 to 6	"
Indigo gluten	2 to 5	"
Ash	3 to 20	"
Moisture	5 to 15	"

The most important of the constituents is indigotin, a dark-blue crystalline powder, subliming at 290° and condensing to prismatic crystals. It is insoluble in most of the common reagents except concentrated sulfuric acid which converts it to sulfindigotic acid (sulfindylic acid, $C_{16}H_8N_2O_2(HSO_3)_2$) believed by some to be a mixture of two acids.

Indirubin is isomeric with indigotin and may be extracted from indigo by hot alcohol in which indigotin is insoluble. When indigo is extracted by napthalene both indigotin and indirubin are dissolved; the latter may be extracted from the former by ether. Under certain circumstances indirubin is converted to indigotin.

Of the various constituents of indigo only the indigotin and indirubin are believed to be of value to the dyer, and so little is known of the advantage or detriment of the others that an indigo test usually comprises only a determination of the two. The percentage of indigotin alone is not a fair criterion of the dyeing quality of the sample.†

Moisture and ash are determined in the usual way. Indigo, both in lumps and powder, is peculiarly subject to hygroscopic changes of the atmosphere; thus, a sample of Kurpah indigo containing originally 11.25 per cent of moisture, showed only 5.15 per cent after standing in a laboratory for seven days at about 75° Fahr.

Many methods have been proposed for the determination of indigotin and indirubin. The best known are summarized as follows.

1. By loss on ignition. In a rapid approximate method there is determined

The process of Heumann for the manufacture of artificial indigo is said to be based on the following reactions.‡

1. Napthaline is oxidized by concentrated sulfuric to phthalic, sulfurous, and carbonic acids—

$$C_{10}H_8 + 9H_2SO_4 = C_6H_4(COOH)_2 + 9H_2SO_3 + 2CO_2 + H_2O.$$

2. Phthalic acid is converted by ammonia to phthalimide—

$$C_6H_4(COOH)_2 + NH_3 = C_6H_4(CO)_2NH + 2H_2O.$$

3. Phthalimide is oxidized to anthranilic acid by sodium hypochlorite—

$$C_6H_4(CO)_2NH + O + H_2O = C_6H_4.NH_2.COOH + CO_2.$$

4. Anthranilic acid is converted to phenyl-glycocoll-orthocarboxylic acid by the action of chloracetic acid—

$$C_6H_4.NH_2.COOH + CH_2ClCOOH = C_6H_4(COOH)_2.NH.CH_2 + HCl.$$

5. Phenyl-glycocoll-orthocarboxylic acid yields indoxyl on fusion with caustic soda—

$$C_6H_4(COOH)_2.NH.CH_2 + 2NaOH = C_6H_4NH.CH_2.CO + Na_2CO_3 + 2H_2O.$$

6. Indoxyl becomes indigo on oxidation by the air in presence of an alkali—

$$2C_6H_4NH.CH_2.CO + O_2 = C_{16}H_{10}N_2O_2 + 2H_2O.$$

* Journ. Socy. Dyers & Col. 1898.

† Journ. Socy. Chem. Ind. 21—222.

‡ Journ. Amer. Chem. Socy. 1901—911.

the indigotin and indirubin by the loss in weight when these are volatilized at a moderate heat. On a flat platinum tray having an area of 14 sq. cm. is spread .250 gram of the finely powdered indigo; the tray is heated on an iron plate just to the point of sublimation of the indigotin, covered meanwhile by an arched hood of sheet iron that the heat may be kept more uniform. When violet fumes cease to appear the capsule is reweighed, the loss set down as indigotin. Against the method is the notable decomposition of both indigotin and the other constituents at the temperature of sublimation.

2. Extraction of indigotin by a solvent. Honig mixes the powdered indigo with fragments of pumice-stone and extracts in a Soxhlet's apparatus with anhydrous anilin or nitrobenzol until the syphonings are colorless. The extraction takes two or three hours. The tube of the apparatus is washed with alcohol, and the anilin distilled leaving the indigotin, which is purified by washing on an asbestos filter with strong alcohol, dried at 110° and weighed.

Brylinski criticises the use of anilin as a solvent, asserting that a certain proportion of the indigotin is destroyed, and that as the indigotin crystallizes it incloses some anilin. He would substitute glacial acetic acid. Brandt admits the destruction of indigotin by anilin, finding that if the indigo be mixed with powdered garnets the action is lessened, but that after extraction for an hour the destruction proceeds rapidly. Concordant results follow when the indigo is mixed with small garnets, sand, etc., and the extraction conducted as rapidly as possible. As a solvent he prefers phenol; on cooling the extract and largely diluting with water containing caustic soda, all the indigotin is precipitated. It is filtered on a tared paper, washed with hot water until the washings become nearly neutral, then with alcohol until it passes nearly colorless. Finally the indigotin is dried at 110° and weighed.

Other solvents that have been proposed are animal oils and napthalin, the indigo precipitated from the extract by ether. Schneider ascertains the loss incurred by the action of the solvent on the indigotin by subjecting the weighed indigotin to the process of extraction under identical conditions with the original and corrects the weight accordingly.

3. Conversion to indigo white. Various reducing agents convert indigotin to a soluble compound known as indigogen or indigo white; thus, ferrous sulfate with calcium hydrate —

$$C_{16}H_{10}N_2O_2 \text{ (indigotin)} + 2FeSO_4 + 2Ca(OH)_2 = C_{16}H_{12}N_2O_2 \text{ (indigogen)} + Fe_2(OH)_6 + 2CaSO_4.$$

The conversion takes place with indigotin suspended in water or with sulfindigotic acid in solution. Since the indigo white is readily oxidized, the reduction must be conducted out of contact with the air, usually accomplished by passing a current of a reducing gas through the flask.

On contact with air, indigo white is reoxidized to indigotin — $C_{16}H_{12}N_2O_2 + O_2 = C_{16}H_{10}N_2O_2 + H_2O_2$ — which, being insoluble, separates as a fine powder.

A weighed quantity of the indigo in a flask fitted with gas-transmission tubes is heated with a measured volume of a solution of the reducer; then an aliquot part is withdrawn by a syphon into a smaller flask. Through this is passed a current of air until the regenerated indigotin is precipitated; the liquid is acidified by hydrochloric acid, filtered, and the precipitate dried and weighed.

Other reducing agents that have been proposed are sodium bisulfite, sodium hyposulfite, grape sugar, metallic aluminum, etc., all in connection with an alkali or earth; Norton recommends zinc dust with lime, and determines the indigotin by drawing the reduced solution into a solution of ferric sulfate, then titrates, by standard potassium bichromate, the ferrous sulfate formed by the reaction between the ferric sulfate and indigogen.

For the analysis of textile fabrics dyed by indigo, Renard directs to treat ten grams of the disintegrated fibers directly with sodium bisulfite and lime.

4. By solution in sulfuric acid and titration by an oxidizer. Indigo dissolves readily in moderately hot, concentrated sulfuric acid. According to Rawson* the best plan for the dissolution of a sample is to mix one gram of the fine powder with an equal weight of ground glass and project the mixture, by small portions and with constant stirring, into 20 Cc. of sulfuric acid of 1.84 sp. gr. held in a porcelain crucible. The mortar is rinsed with a little powdered glass, and the crucible heated in a water-oven for an hour to 90°. The solution is cooled, and diluted with water to one liter.

For the titration with permanganate, the solution is filtered and 50 Cc. drawn into a porcelain dish and diluted with 250 Cc. of water. A standard solution of permanganate is run in until the color of the titrate passes from greenish to light yellow denoting the complete oxidation of the sulfindigotic and sulfindirubic acids to sulfisatic acid—

$$5C_{16}H_8N_2O_2(HSO_3)_2 + 2K_2Mn_2O_8 + 6H_2SO_4 = 5C_{16}H_8N_2O_4(HSO_3)_2 + 2K_2SO_4 + 4MnSO_4 + 6H_2O.$$

The standardization of the permanganate is made on pure indigotin dissolved and diluted as above.

Since permanganate is also reduced by other constituents of the indigo soluble in sulfuric acid, it is recommended that before titration these be removed by salting out the sulfindigotic and sulfindirubic acids, which after filtering are dissolved and titrated. Barium chloride has also been recommended for purification. Donald and Strasse would purify the indigo before sulfonation by successive extractions with water, hydrochloric acid, alcohol, and ether.

In lieu of permanganate the oxidizer may be potassium ferricyanide which in alkaline solution forms isatin or indigotic acid, or potassium bichromate in acid solution, but neither of these has any marked advantages over permanganate.

5. By reduction. Strong reducing agents convert sulfindigotic acid to the nearly colorless compound disulfo-leukindigotic acid. The determination is made volumetrically by sodium hyposulfite ($NaHSO_2$) in a current of some non-oxidizing gas. The titrand is standardized against pure indigotin dissolved in sulfuric acid and diluted. Mueller claims that indigo-red, indigo-brown, and indigo-gluten are not reduced by this reagent. This reaction is

$$C_{16}H_8N_2O_2(HSO_3)_2 + NaHSO_2 + H_2O = C_{16}H_{10}N_2O_2(HSO_3)_2 + NaHSO_3.$$

Indigotin is reduced quantitatively by vanadyl sulfate, vanadium dioxide (V_2O_2) being oxidized to the pentoxide (V_2O_5). The titrand is made by dissolving ammonium vanadate in sulfuric acid, diluting the solution and reducing by zinc powder. The titration is carried out in a current of carbon dioxide, the end-point being the disappearance of the blue color of the sulfindigotic acid.

6. Various other methods have been proposed. Gerland removes other constituents by converting the indigotin and indirubin into their *mono*-sulfonic acids by vitriol of 1.67 sp. gr.; on dilution with water these are completely precipitated. After filtration the precipitate is treated with acid of 1.84 gravity which produces the *di*sulfonic acids, determined by titration. Voeller purifies indigo by successive treatments with hydrochloric acid, sodium hydrate, alcohol, and water, then determines the nitrogen in the residue by the method of Kjeldahl; the indigotin is calculated from the formula $C_{16}H_{10}N_2O_2$.

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* Journ. Socy. Dyers & Col. 1—75.

7. For a determination of indirubin, Gardner and Denton boil .2 gram of the powdered indigo with 100 Cc. of acetone under a reflux condenser. The liquid is then made up to 200 Cc. with a ten per cent salt solution, this precipitating any traces of indigotin that may have dissolved. After filtration through asbestos, the filtrate is compared colorimetrically with pure indirubin treated as above. The residue of indigotin is washed free from salt by hot water, dried, dissolved in sulfuric acid, and determined by titration with permanganate.

8. The dye-test can be made by grinding one gram of the dried indigo with five grams of glass, then extracting successively by hot dilute hydrochloric acid, hot dilute solution of sodium hydrate, and hot water. The dried residue is dissolved at 100° in sulfuric acid of 1.85 sp. gr., the solution diluted with water, and made up to one liter. A special form of apparatus has been described by Grossman.*

As to the relative merits of the various processes there is some difference of opinion. The conclusions of Rawson† are given below, though it must be recognized that his views on several points are not concurred in by other authorities.‡

"2. The permanganate method affords a quick and ready means for the approximate valuation of indigoes, but as substances soluble in dilute acids are, at the same time, more or less acted upon, the results obtained are somewhat too high.

3. If the solution of indigo be saturated with sodium chloride, the colouring matter is thereby precipitated. When the precipitate is washed, dissolved in dilute sulfuric acid, and titrated with potassium permanganate, results are obtained that for all practical purposes are trustworthy and reliable. Indigo-red and indigotin are simultaneously estimated by this modified process.

4. Of all the volumetric methods which have been devised for estimating the indigotin, the sodium hyposulfite process is capable of giving at the same time the quickest and most accurate results; but as previously stated, considerable care and delicacy are required in its manipulation. If the solution of indigo to be titrated with hyposulfite contain iron in the ferric state, then the result obtained will be too high.

5. Other bodies than indigotin which are present in indigoes are more or less affected by the process of sublimation, while indigotin itself is partly decomposed into a dark brown substance, which does not volatilize without complete destruction. According to the quality of indigo the results obtained by this process may be either too high or too low.

6. The gravimetric reduction processes as commonly described are not quite so accurate as is generally supposed. Perfectly reliable and accurate results are, however, obtained by the use of sodium hyposulfite and lime water. The reduction is complete in less than half an hour. Where an exact chemical analysis is required, this method I consider gives the best results of any process which has hitherto been published."

A large number of analytical schemes for the identification of dyes in dyed fabrics have been described.§

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* Journ. Socy. Dyers & Col. 1897—124.

† Chem.-News, 51—256.

‡ Journ. Socy. Dyers & Col. 1896—96, and 1897—124.

§ Journ. Anal. Chem. 1—440; Journ. Socy. Dyers & Col. 1898—210; Prescott Org. Anal. 182; Analyst, 1899—41.

PART 4.

NOTES ON THE METHODS OF ANALYSIS.

NOTES ON THE METHODS OF ANALYSIS.

The development of the art of quantitative analysis may be credited on the one hand to the extension of qualitative analysis, and on the other to the adaptation in miniature of technical processes.

Probably the earliest attempt at a quantitative analysis was of the nature of a fire-assay of the ores or alloys of the precious metals; for the reproduction on a small scale of the crude processes of extraction and refining known to the ancients would be readily suggested to those engaged therein. From this inception the art grew by small accessions, traceable in the writings of the alchemists and their followers, and extended in succession to other useful minerals and ores, the compounds of the common metals, the inorganic acids, the ultimate constituents of organic bodies, the rarer metals, and finally to general proximate analysis. Of an art so interwoven with others and so eminently one of detail, it is idle to speculate as to whom belongs the honor of being the founder; of the three or four that have been named, all have undoubtedly made most important contributions, but a firm foundation had been laid prior to the time of the earliest.

The art in general and particular, has been materially advanced at various times by the discovery of leading principles and the invention of appliances for facilitating the practice. Of these may be mentioned the principles of volumetric analysis, gasometry and electrolysis, the application of the polariscope, colorimeter and dephlagmator, the invention of the deluminated gas-burner and the vacuum filtering apparatus, the construction of platinum utensils, and others of less conspicuous advantage.

Another factor has been the progress toward precision in the valuation of such physical constants as are concerned in the calculations of analysis. The atomic weights on which depends the accuracy of nearly every chemical analysis have been corrected to such a degree of exactness that the errors introduced are inconsiderable even in the most refined investigations. And reliable determinations of constants of more special application have admitted several purely physical methods to the resources of the analyst, frequently to supplant chemical methods more intricate or less accurate.

Again, the assistance afforded by the continuous advance in the way of increasing the variety and improving the quality of the appliances for chemical work can not be overestimated, for the manufacturer has well kept pace with the ever increasing demand. The precision-balance of today is a most exact, reliable, and withal, low-priced instrument, and the accompanying weights remarkably accurate; glass and porcelain vessels are at hand convenient in form and well resisting the corrosive action of chemicals, platinum wrought to almost any desired shape, and physical instruments and volumetric ware of high precision. And one cannot but appreciate the skill of the glass-blower as he fashions the most intricate forms of apparatus, making possible many chemical operations that otherwise could be conducted only with difficulty if at all. In the equally important requisite of reagents, chemicals are now supplied in large variety, of guaranteed purity, and at a reasonable price. Surely the readiness of the manufacturer to meet or anticipate the wants of the chemist may not infrequently be accredited to a loftier motive than mere business thrift.

But as a whole the practice has been built up mainly by accretions of minor importance, the outcome of patient and persistent efforts in the direction of instituting and perfecting particular methods of analysis; widening their scope when possible to include other than the special classes of bodies for which they were originally designed, or, on the other hand, so modifying the details—here by the omission of a superfluous feature, there by the introduction of a measure tending to greater simplicity, accuracy, or dispatch, or a precaution against an avoidable source of error—as to adapt them for special work calling for exceptional rapidity or many analyses in a limited time. To these extensions a great impetus was the publication of the works of Rose and Fresenius, the first monographs of methods for the systematic examination of inorganic bodies and practical directions for manipulation.

A feature that has had a marked influence on the advance of the art is the unreserved manner in which analysts in general have made public the discoveries and inventions they have considered of interest to their fellows. Particularly is this to be commended of specialists whose extended study in one single department of analysis constrains respectful consideration of the views they advance. A few are more reticent, defending their secretiveness on the plea of fidelity to employers or clients, or that the publication of certain methods of analysis in detail might give information to those who would profit by it for illegitimate ends, as for adulteration or counterfeiting. But the mutual benefit to be derived from a free interchange of experiences and opinions is so generally recognized that a claim to the possession of a secret method superior to any that are common property may well be regarded with suspicion. And in the rare instances where a patent has been secured for an analytical method, it is probable that protection was sought, through establishing priority, for any technical processes that might be founded thereon, rather than the right to control its analytical use.

Glancing at the present status of the art, how far and along what lines it has been developed, it may be premised, first that the accuracy and ease with which an analysis can be made—outside of the physical methods—are in a measure correlative with the chemical activity of the constituents determined, for the more positive and pronounced the relations of a body toward reagents, the more likely are the methods for its determination to be numerous and satisfactory: and, second, the fact that the determination of a body will further some practical end or prove a financial advantage is always a stimulus to the invention and perfection of methods therefor. For these and other reasons, the elementary bases of the common inorganic compounds and the organic tetrad have received the most attention. For some elements and compounds we have a choice of a number of methods all reasonably accurate and generally applicable, while for others are limited to a few or but one, often tedious and unsatisfatory at best. And it is not uncommon that a method will answer the purpose when prosecuted under the conditions detailed by the originator, yet be unreliable when these are departed from even but slightly.

Most of the common metals can be determined with great or at least reasonable accuracy and by a number of methods, and their separation from accompanying bases and acid radicals presents no great difficulties. With a few of the more chemically indifferent the methods are complicated and not overexact. Of the rarer metals, on the contrary, but comparatively few can be determined with any assurance of accurate results, owing chiefly to the difficulty of separating from the various groups the individual members whose reactions show great similarity.

Of the inorganic acids, the mono-sulfur oxides and the halogen radicals offer no particular obstacles to an accurate determination; phosphoric acid is rather more troublesome from the necessity of a previous separation from most bases; while the determination of boracic and hydrofluoric is not an easy task, and nitric still lacks one simple convenient method. Associated oxygen compounds of nitrogen and of the halogens, and the thionic radicals can only be determined indirectly or through somewhat equivocal oxidations or perductions.

Thanks to the labors of Bunsen and his followers, the proximate analysis of mixed gases has been brought to a degree of accuracy scarcely inferior to a refined gravimetric analysis, and with few exceptions the simple and compound gases can be determined with exactness, or with great rapidity where a slight inaccuracy is not unallowable.

Ultimate organic analysis has been developed to a degree that leaves little to be desired in point of exactness, but requires complicated apparatus and unremitting attention throughout the process of combustion, and only after considerable practice in the routine can one place confidence in his results.

Although proximate organic analysis offers what is perhaps the most interesting and profitable field to the analyst, yet as compared with other branches it is at present the least developed. Among the analytical difficulties are that many of the multitude of known organic bodies are closely related in ultimate composition, though differing widely in habitus and physical properties; that many compounds easily degenerate to decomposition products, either spontaneously, on exposure to the air, or by contact with the reagents during the course of the analysis; that in mixtures of allied complex bodies the identity of the members may be wholly lost; and that comparatively few form combinations sufficiently insoluble to be utilized for a separation. The determination of the various organic groups composing a molecule, necessary for the identification of a compound, can be done with sufficient accuracy in many cases, but often the normal reactions are interfered with or entirely annulled by variations in the configuration of the molecule or the modified behavior of substituted groups.

The strictly quantitative methods that are available for organic bodies are few in comparison to those for inorganic analysis, since for the latter the usual reagents have in general a broader application, a given reagent being suited, as a rule, to most or all the combinations in which the element or radical to be determined may enter, though for practical reasons but one form of combination may be best suited for the purpose of analysis.

Of the multitude of organic bodies comparatively few unite with reagents to form precipitates sufficiently insoluble and stable to admit of filtration and drying, and their direct determination is therefore limited to the plan of evaporating their solutions to dryness and weighing the residues, a scheme often equivocal in view of the ready volatility or decomposibility of many varieties. Sometimes a fair result can be arrived at through an indirect or physical method; if of a pronounced acid or basic character or if readily oxidized or reduced or otherwise transformed, a volumetric method may be availed; and a number form measurable decomposition products with certain inorganic bases, ferments, strong oxidizers, etc. In most cases the difficulty of a separation and determination is greatly increased where the body forms but a small proportion of the mixture analyzed, this feature more evident here than in inorganic analysis.

On the whole, it may be said that reasonably accurate results are possible with only a minority; fair results are obtainable with many, and approxima-

tions with more; while not a few can only be estimated by difference, and in mixtures of allied bodies all that can be hoped for is the fair isolation of the respective groups, falling back on indirect means to identify and determine as far as may be, the individual members.

Of the more familiar organic bodies, most of the acids form precipitates with the earths and certain metals, the insolubility being sufficient for a fair determination; those that are volatile at moderate temperatures without decomposition may be distilled — if combined with a base, after displacement by a non-volatile inorganic acid — and determined in the distillate by acidimetry.

Of the organic bases, the vegetable alkaloids admit in most cases of moderately close, at times highly accurate determinations, since like their inorganic archetypes, they form fairly insoluble compounds with a number of reagents. But when only a minute amount is mixed with a large proportion of other organic matter (*e. g.*, in toxicological examinations), one may be well satisfied to obtain a distinct and conclusive qualitative reaction. The same is true of the animal bases — the amines, amido-and imido-compounds, xanthins, pyridins and urea and their analogues and derivatives, etc., which have for the most part the character of moderately strong bases, a few reacting as a base or an acid according to circumstances.

The carbohydrates show relatively little chemical activity toward reagents. For the separation of the sugars, differences in solubility may be availed, though the determination is usually made by a physical method, decomposition by a metallic salt, or fermentation. The starches may be separated from accompanying soluble matter by cold water, but a determination usually follows the conversion of the starch into sugar and the determination of the latter. From their insolubility and resistance to most reagents, the celluloses form the final residue in an analysis, though attempts to separate retained impurities generally result in the loss of part of the cellulose as well.

The alcohols of low boiling points are separable from less volatile associates by distillation, easiest by distillation with water; usually the specific gravity of the water-alcohol distillate is a sufficiently accurate means of determination. Oxidation methods are complicated by commonly occurring associates difficult of separation, and by the relative stability of members of this group. The higher alcohols, including glycerol, phenol, etc., form some definite combinations with other bodies that admit of a fair determination, but physical methods are generally preferred.

Similarly, the lighter ethers are separable from fixed bodies by distillation, and may usually be obtained in a nearly pure state and weighed or measured. The heavier bodies of this class can be extracted from a solution by a solvent immiscible therewith. The compound ethers admit of saponification and determination by the weight of alkali entering the decomposition products.

For the fats and oils hydrolysis offers not only a means of direct determination and separation from unsaponifiable matters, but the decomposition products possess certain physical properties that may be taken advantage of for identification and further examination. For the rest one must rely on the divergent values of physical or chemico-physical constants of the oils. The indifference of the mineral and rosin oils to reagents that act on those of animal or vegetable origin may allow their isolation, while the more volatile members can be distilled as a whole or fractionally. Many of the essential oils combine wholly or in part with reagents to form determinable decomposition products; like the lighter mineral oils, they are separable from fixed

associates by distillation with water; various attributive methods are frequently applicable for their determination.

For the tannins have been proposed a very large number of methods—"several hundred" (*sic*). They form precipitates with a number of metallic bases but of such indefinite composition and so readily decomposed that the combining weights are not deducible with certainty. Hence, notwithstanding the labor of many investigators, there are but two, perhaps three, possibly four methods that have gained the confidence of chemists. The members of the tannin family are closely allied in deportment toward reagents, and a separation is impossible in most cases. None of the methods can lay claim to determine tannin *solus;* at best there is only indicated the proportion of an indefinite group of bodies that exhibit a peculiar behavior toward the albumins and similar bodies.

The organic dye-wares have up to the present time been assayed mainly by colorimetric methods or comparative dye-tests, and even the anilin dyes whose composition and molecular arrangement is so well understood and whose chemical attributes are so decided, seem to have been neglected in the search for assay methods.

Several schemes afford a fair separation of the various proteids by fractional precipitation.

Finally there is the large number of organic bodies for which no satisfactory methods of separation and determination are known, many of these familiar from their use in the arts and domestic economy.

The qualities that most commend a method of analysis are accuracy, simplicity and rapidity, though but exceptionally does a method associate the three, and many can claim neither, retained only for want of others more meritorious.

The relative importance of these qualities toward a given analysis is dependent on the object for which the analysis is made and the deductions to be drawn from it. In scientific investigations and in certain classes of technical analysis the highest accuracy is paramount to all other considerations, and methods are adopted with this object in view. On the other hand, for most technical analyses usually the highest accuracy is not insisted on and may with advantage be subordinated to other qualities.

In industrial analyses it is usually left to the discretion of the chemist as to the standard of accuracy to be maintained in his routine examinations, and in establishing such standards he must be governed by several considerations. Thus, with such items as purchases and sales on a guaranteed basis of purity nothing short of the most exact results attainable should be allowed to pass; on the other hand, in dealing with by-, intermediate, and waste products and the like, a much lower standard may be adopted without impairing the practical value of the results. Again, if highly or even fairly accurate results are to repay the necessary time and care bestowed, among other requisites there must have been a correspondingly accurate sampling of the material analyzed, and the analytical results must be capable of being interpreted or practically applied within the limits of error. For it seems but farcical to labor for refinements in the analysis of a sample that may be far from a representative of the original; nor is it more defensible if the same conclusions would be drawn or the same disposition made of the material though the results differed to a degree many times greater than the presumed maximum inaccuracy. Finally, if circumstances decree that the

analytical work be done by those unacquainted with the principles of chemistry and without training in general analysis, as is the policy in some industrial laboratories, an attempt at high accuracy is futile if attainable only by abstruse schemes and complicated forms of apparatus.

The degree of accuracy that may be attained in a given determination depends primarily on the excellence of the method of analysis. A method for the determination of an element or compound may fall into one of three classes.

1. The first class includes those which combine all the various qualifications essential to exactness and are suitable for the most refined research work. The class is comparatively small and, the methods, unless based on specific reactions, usually complicated and tedious.

Following the lines of quantitative analyses are the determinations of the atomic masses, a task calling for a degree of care and nicety beyond that of any other investigation. The element itself or one of its compounds taken as the basis, and all the reagents used in the determination require most thorough purification; the balance and weights must be of the highest precision, and the weighings so conducted as to minimize the defects inherent to even the most perfect instruments; every source of analytical error must be searched out and provided against; and the final product proven beyond a doubt to be exactly of the assumed composition. And as all these precautions may be subverted by a slight error in manipulation, the simplest methods involving the fewest mechanical operations are always to be preferred.

A favorite method for the metals is to weigh a suitable quantity after elaborate purification, and convert it into the most stable oxide by some simple process, as by heating in oxygen. Another combination might as easily be formed, such as the sulfide, but here the atomic ratio of sulfur to the basis of the system (oxygen or hydrogen) enters the calculation with whatever uncertainty attaches. Several determinations, if possible by different methods, are always made, and if the results of a number of chemists of repute agree with reasonable closeness, the average of all is probably very near the truth — always admitting the possibility of an undiscovered common error.

Methods of this class are also applied for the analysis of chemical compounds to determine or corroborate the empirical formulae. The formula as deduced from an analysis is the more defensible the nearer the results harmonize throughout with the composition as calculated from the assumed formula. This, of course, on the presumption that the compound as submitted to analysis was in a perfectly pure condition, or at least practically free from other bodies. But as the probable errors in the several determinations usually differ more or less, it is necessary to assume an approximate probable error in the determination of each element and draw conclusions accordingly.

2. Comprised in the second and by far the largest class, are those associating reasonable precision with general applicability and ease of working. They are usually qualified for the analysis of well-known natural bodies or staple articles of commerce, and are generally planned for the separation and determination of the constituents normally contained therein, not providing for any that are exceptional, accidental, or derived from foreign sources.

As to what shall constitute the limits of inaccuracy conformable with 'reasonable precision' in this case depends as much (sometimes more) on the skill and care of the operator as on the method. However all will agree that several analyses made by one such method on one sample by one chemist

should yield results all within the allowable limits of inaccuracy as fixed by analogy and common experience.

3. Lastly, there is a class of highly specialized methods planned for one material only with conditions of the practice rigidly fixed. Like those of the preceding class they are restricted to the combinations in which the body determined is commonly found, and are planned for separation from only the usual concomitants; moreover as a rule their successful working is contingent on the absence of certain other bodies, this presumed from the nature or origin of the substance, and confirmed if any doubt exists, by qualitative tests. They are characterized by simplicity and rapidity, qualities highly appreciated in industrial analysis for which they have been chiefly devised. In this class fall also those methods that are simply attempts at following some particular division of a technical process along lines as near to it as conditions allow.

Many of these methods have been adapted from others more accurate by so modifying the procedure as to materially reduce the time required for their prosecution. The desired rapidity may be secured by hastening the operations of a gravimetric analysis regardless of small losses entailed; *e. g.*, by quickly boiling down a solution to dryness instead of evaporating at a moderate heat; for the slower process of the filtration, ignition and weighing of a granular precipitate may be substituted the (less accurate) one of measuring its volume. Broadly, a reaction may be accelerated by so arranging matters that the conditions for the exhibition shall be most favorable, excluding or removing whatever tends to retard its incipience or completion.

Volumetric and colorimetric methods of this kind are, as a rule, much more rapid than gravimetric, and may be still further shortened by various simple expedients; as by the use of empirical standard solutions of such concentrations that, upon a fixed weight of sample, the percentage of the constituent will be shown directly by the number of cubic centimeters used in titration; colorimetric comparisons facilitated by series of standards or means of comparison; etc.

Physical or attributive methods can be applied only after verifying the noninterference of other constituents of the substance normally or exceptionally present, though it is often possible to deduce and apply a correction for the effect of an associate found in a practically constant proportion to the constituent determined. Of the various physical characteristics that may be utilized, specific gravity is most often available.

In defense of methods of this class it may be said that their rapidity allows a control of technical and manufacturing processes not practicable with methods requiring a longer time; even a method that is conceded to give only approximate results may be of great practical service in this way by indicating the suitable subsequent treatment of a material in progress of conversion. Again, in the case of some organic mixtures, only rapid methods can be used on account of the proneness of the material to decomposition by oxidation or fermentation. Usually the maximum error likely to be incurred in the ordinary practice of such a method can be predetermined and allowed for in drawing deductions and applying the analyses, and in designing one it is often possible to so arrange the details that a probable plus error at one stage will be in a measure counteracted by a minus one at another.

Against them may be charged that although inherent errors can be obviated or corrected for by observing specific directions, yet the details are not always easy to follow without undivided attention and the neglect of other analytical work carried on at the same time; that while in technical analysis a result indicating that the particular sample under analysis is of abnormal com-

position at once suggests the advisability of corroboration by a more accurate method, yet should an abnormal material be returned as of normal composition the error would probably pass unnoticed; finally it cannot be denied that some, perhaps many, of such methods are liable at times to give erratic results without apparent reason. In any event caution in the adoption of methods of this class and in the acceptance of their results is the part of prudence.

Usually the saving of time due to these methods is most manifest where a single analysis or but a few are made at one time, and may quite disappear where a considerable number of determinations are begun and carried along together

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At times one may be at a loss to select from a number of unfamiliar methods the one that will answer best for a given determination. A choice will be aided by a consideration of the object for which the analysis is to be made, this determining not only the degree of accuracy to be aimed at, but helping to decide questions in regard to other matters that may arise before or during the analysis.

The chemist may feel free as to a choice of methods to be used for analyses made only for his personal information or in the course of investigations of a specific or confidential nature, but when his results are to be published, in scientific investigations, or in the valuation of merchandise, or when acting as an expert or umpire, he will be wise to regard not only his own convictions, however positive they may be, as to the best method to be adopted or what details are most expedient, but the consensus of opinion of his fellow-workers as well, and modify his practice to conform, in some degree at least, to the prevailing practice of his professional brethren. Especially is this concession appropriate with the more arbitrary methods where details are so much in evidence.

Out of the host of methods that have been proposed, some have come into general use, others dropped into comparative obscurity. The survival of the fittest will in part account for this election, but he who searches chemical literature will not fail to discover many that are apparently correct in theory and highly practical, but of which he can find no mention in the works on special branches of analysis, or at best are dismissed with but a brief and equivocal comment.

A method devised and published may be so palpably superior to others in common use as to meet with immediate favor and supplant to a great extent all previously in use. The superiority may not be in the way of accuracy alone, but by reason of comparative rapidity or convenience may meet with favor and take precedence over those perhaps more accurate but less suited to the technical chemist.

On the other hand, a method may offer some advantages over those in common use yet not sufficient to gain general adoption. One does not readily turn from a well-tried method with whose details he is familiar, knowing the routine best suited for his purposes and most practicable with his facilities, its limitations and weaknesses where caution is demanded, its adaptability and trustworthiness, to one offering but little in exchange for the risk of a failure where his reputation might suffer. Rather would he defer the change until the high opinion of the deviser was supported by others in whose impartiality and judgment he could place confidence.

Again, many methods have not received the favor they deserve solely for the reason that in the original description or abstracts some detail of vital importance has not been sufficiently emphasized, and the first trial being unsatis-

factory on this account has led to a depreciation and abandonment of the method.

Another and common reason for neglect may be that the original publication appeared in a technical or trade journal of very limited circulation among chemists, and has therefore escaped the notice of both the majority of chemists and of the abstracters for chemical journals.

As a general proposition, the most serviceable method is one that is free from any considerable inaccuracy in principle or practice, and does not demand many or delicate operations or an excessive time for its prosecution. In most departments of special analysis there will be found one or more methods that answer these requirements at least fairly well and have been generally accepted by specialists, and may be adopted with confidence by those less familiar with the special subjects concerned.

Let us consider to what standards a quantitative method may reasonably be expected to approach.

GRAVIMETRIC METHODS.

A gravimetric determination has the advantage over most others in that it is direct and positive in character; at the same time there is afforded the opportunity of preserving the products and educts for examination should there be suspected an imperfect separation or contamination from other sources or an error in weighing. A gravimetric method of the highest order should

1. Be free from all avoidable sources of error.
2. Allow a considerable departure from any specific directions laid down without impairing the accuracy.
3. Be equally applicable to every percentage, small or great, of the constituent determined in the substance analyzed.
4. Assume no manipulative skill beyond that of the average chemist, and call for but few reagents, and these neither rare, expensive or difficult of purification, and not require forms of apparatus that are complicated, cumbersome, or of a special character.
5. Provide a means of separation for each constituent that will not prejudice the subsequent determination of others — this, of course, does not apply to an assay only.
6. Provide that the precipitate or residue finally weighed be of a perfectly definite composition, and neither unstable, volatile, hygroscopic, efflorescent, or liable to hold occluded or adsorbed matters, and preferably containing only a small proportion of the body determined.
7. Not require an unreasonable time for its performance.

Very few methods will be found that comply literally with all these requirements, though none can be deemed too exacting.

As a rule, a quantitative method is designed with a view to the analysis of some distinct substance or class of substances wherein normally the proportions of the constituents do not vary from the typical composition to any great extent, and must be modified beyond increasing or diminishing the amount of substance taken for the analysis, or adjusting the quantities of the reagents, when dealing with those deviating beyond certain limits. Often it will be found that an effective separation of two constituents by a given method is only successful when their relative proportion is within a certain limited range.

Usually a method specifies the order in which the constituents are to be separated, but this may often be changed with advantage. In deciding the most advantageous sequence there are to be taken into consideration:

1. Their relative importance, assigning priority to any one on whose propor-

tion the value or utility of the substance under examination is based, as being earliest separated, it is subject to fewer operations with their attendant errors. And where a delicate or tedious process must be gone through with, it is better that it be performed as early in the analysis as possible, for at that period is the best work likely to be done. By force of will one may exercise equal care throughout an extended analysis, but the natural tendency is to become less circumspect as the work draws to a close — at times the diminuendo is painfully in evidence.

Against the above must be weighed, of course, the possibility or certainty of interference with subsequent separations.

2. The generic or specific type of the reagents used. Group reagents, those reacting with all the members of a certain class of bodies, are less often employed than in qualitative analysis. An objection is that the precipitates formed from the reactions with the different members have not the same coefficient of solubility in the supernatant fluid or the washing medium, and the separation from the members of another class will seldom be as complete as if specific precipitants were applied in succession; on the other hand the latter plan has the disadvantage of loading the liquid with the excess of the precipitants and soluble products of the reactions.

Another reason for preferring a specific precipitant is that the product of the reaction is usually left in a form that allows direct weighing or measurement, while a group reagent implies at least one other separation of the conjointly precipitated members.

The completeness of separation of a pulverulent mixture by a given solvent depends primarily on the ratio of the solubilities of the constituents therein, but other influences cannot be ignored. These may be: (1) mechanical, as where the particles are in such a physical condition that easy permeation is not allowed; or the soluble constituents may be or become enveloped by the insoluble parts and shielded from contact with the solvent, and this however well the mixture be agitated during the treatment, or the digestion prolonged. If the mixture is not in fine subdivision, the soluble constituent should not be in less than a certain proportion in the mixture, a specific ratio determined by the physical structure and density of the components and other considerations. (2) A soluble and an insoluble constituent may unite on contact with the solvent to a form not decomposed by it and remain insoluble. (3) A solid when pure may be unaffected by a given solvent, but when diluted with another solid may dissolve perceptibly, largely, or entirely. (4) In the separation of two liquids, often the solubility of the one more insoluble is increased to a remarkable extent by the presence of the other in the solvent, and many erroneous statements as to the purity of commercial articles may be traced to a disregard of this peculiarity. The phenomenon is oftener observed in a separation by a group reagent than when specific reagents are applied in succession.

3. The liability of the presence of the residual radical of the body separated or the excess of the reagent to interfere with succeeding separations. For this reason many organic reagents are disqualified for inorganic separations, though otherwise most efficient for the purpose.

4. The proportion of the constituents to each other. Two bodies of similar chemical attributes may often be parted with ease when the ratio of their weights is a small number, yet difficulties be met when one greatly predominates; a familiar example is that of the alkali salts of sea-water, the sodium chloride exceeding the iodide a thousand or more times. Exceptions to this rule are found in some organic bodies closely allied in chemical character (*e. g.*, catechol and pyrogallol), where the separation of a mixture of approxi-

mately equal proportions is more difficult than when one greatly preponderates.

In the analysis of a material of which one constituent forms nearly the whole, the determination of the others will be much facilitated if it can be removed at the outset by a specific reagent, some physical process or otherwise. Thus, for the analysis of a commercial metal there may be found a specific solvent that will dissolve all or the greater part of the major constituent leaving the impurities; the latter may either be insoluble in the menstruum or dissolved only after all the major constituent has passed into solution. Less often can a specific solvent be used to extract the basis of a commercial salt, since the common impurities usually show a similar behavior toward solvents.

Or a specific precipitant may be found that will unite with the chief constituent to an insoluble compound, the impurities likely to be associated being freely soluble and afterward easily separated from the small amount of the former remaining in solution. Instances are the precipitation of lead from the commercial sugar of lead (the crystallized acetate) by sulfuric acid, copper from the raw metal by a sulfocyanide and sulfite, tin from sodium stannate by evaporation with nitric acid, etc.

Conversely, there may be applied a solvent that will withdraw the impurities, at least in great part, leaving the leading constituent insoluble. But for physical reasons this method is inferior to the former. Similarly a precipitant (or a mixture of several) may sometimes be found that will throw down most or all of the impurities with none or but little of the major constituent.

In default of a better plan, the greater part of the principal constituent may be isolated by fractional solution, distillation or crystallization, by congelation or fusion, etc., though the separation is never better than approximate.

In the determination of a body by precipitation it is presumed that the precipitate can be freed from the excess of the precipitant or other bodies present in the solution by the process of washing with a suitable liquid. But however thorough the washing, a precipitate may remain impure from at least four causes.

A. Some secondary reaction may result from contact of the supernatant fluid with the air or laboratory gases, the decomposition of organic matter, or other cause, with the formation of an additional precipitate insoluble in the washing fluid.

B. Matter suspended in the solution is entangled and carried down more or less completely according to the consistency and bulk of the precipitate. By a glairy or gelatinous precipitate a liquid may be clarified of a suspended powder so finely divided as to pass through the pores of an ordinary filter paper.

Quasi-soluble or colloidal bodies in unstable solution may be influenced to assume an insoluble form by contact with a precipitate, perhaps by a force analogous to the promotion of crystallization by seeding.

And freely soluble bodies may be retained in small amount — be it through the formation of a double salt, be it in a mechanical way only, nevertheless they are held so tenaciously that protracted washing will not remove them. Gelatinous metallic hydrates, for example, are freed with difficulty of alkali salts by washing with water (though quite easily after a change in structure has been induced by drying or freezing), and considering their consistency such a tendency is not surprising — witness the 'lakes.' With dense granular precipitates occlusion would not be expected, yet instances are not uncommon; manganese binoxide, precipitated from a hot nitric solution has a marked attraction for the nitrates of other metals, and when thrown down electrolyt-

ically, occludes iron compounds; barium chloride in aqueous solution is not completely decomposed by sulfuric acid, the precipitate always containing a small amount of barium chloride even when the sulfuric acid is in large excess, the solution dilute, and the mixture heated to boiling; etc., etc.

That this phenomenon is not always simply a mechanical inclosure is argued, among other evidence, by the unequal amounts in which analogous bodies are retained. Thus, Schweitzer,* in determining the sulfuric radical combined with various metals, precipitated solutions of their sulfates by barium chloride and, after thorough washing, weighed the barium sulfate; on potassium sulfate he obtained 99.32 per cent of the calculated weight of SO_3, and on sodium sulfate 100.18 per cent, showing clearly that potassium sulfate is occluded in the precipitate to a greater extent than sodium sulfate. Similarly, barium sulfate precipitated in presence of ferric chloride always contains more iron than if only ferrous chloride is present, perhaps from the formation of a ferric barium sulfate. In general it may be said that the compound predominating in the solution during the precipitation is the one most occluded, hence the usual order of pouring the precipitant into the solution to be precipitated may sometimes be reversed with advantage.

A simple and effective means of insuring the purity of a precipitate and one ordinarily available, is that of redissolving it after filtration and washing and repeating the precipitation; here the soluble associates, largely removed in the first operation, remain in so comparatively small proportion that practically none are carried down. Occluded bodies are best eliminated before a precipitate is weighed, but where this is not practicable a subsequent purification should be attempted only by a method of the simplest nature; many of the schemes proposed for the purification of ignited precipitates are likely to entail losses or introduce impurities in greater weight than those sought to be eliminated.

It is plain that the correctness of a gravimetric determination made in the usual manner depends primarily on a fixed and invariable relation of the weight of the element or compound determined to the product weighed. In inorganic analysis generally, the relation is a constant, but in organic determinations frequently the reaction or reactions are so incomplete, indefinite, or complex, intricated by secondary reactions, conditions of precipitation, etc., that it varies to a considerable degree. Nevertheless a method based on such a reaction may be employed with fair results if admitting of a correction; thus, (1) if the reaction be incomplete or reversed to a certain definite extent, a simple multiplication by a coefficient deduced by experiment; (2), if also influenced by conditions of temperature, duration of contact with the solution, and the like, the analysis is conducted under the same conditions as in the determination of the coefficient; (3), if the relation varies directly or inversely with the weight of the element or compound to be determined, an equation of the form $P = aW + bW^2 \pm cW^3 \ldots$ or a simpler one may be deduced and applied; and (4), the extent of some physical property of the filtrate or its concentration may serve to fix the proper correction.

Again, the rule as usually stated that the compound finally weighed or measured shall be of a definite chemical composition, includes both polymers and metamers, and may be broadened to require only that it shall contain a definite proportion of the element sought, thus covering a mixture of two compounds, both holding the same proportion of a common element or compound though

* Catalogue State Univ. of Missouri, 1876.

united with different radicals. Conventionally, a mixture of two or more analogous compounds too small in weight to admit or to justify separation is returned as of the composition of the one predominating; the same applies in technical analyses where two associated bodies are equally important or commercially valuable.

Of the other requisites, a precipitate that may be ignited is preferred, as the alternate process of drying at or below the temperature of 100° is tedious at best and often less accurate. Very hygroscopic bodies need so careful shielding from the air and must be weighed so rapidly that it is better to change the form to one less hygroscopic even at the expense of an extra precipitation. With solid or liquid bodies that are volatile at 100° or below a certain loss is inevitable on drying or evaporation, and there is often no way by which to transform them to non-volatile compounds. The loss may be kept within bounds by arranging for their solution in a highly volatile solvent and conducting the evaporation at a lower heat, weighing the residue as soon as the solvent has gone.

The smaller the proportion of the element sought in the compound weighed, the less will equal errors of weighing, etc., affect the result. This is well illustrated in determinations of nitrogen (molecular weight 28) and platinum (atomic weight 194.89), both weighed in the combination of ammonium platinic chloride (molecular weight 443.654).

VOLUMETRIC METHODS.

Contrasted with the many approved methods of gravimetric analysis, but comparatively few volumetric methods are available, the reasons lying in the following requirements.

1. A single reaction, definite and preferably instantaneous. If one of the reaction-products is insoluble, the precipitate must have no tendency to occlude the yet unprecipitated active constituent.

Instead of a single reaction, another may occur simultaneously or asynchronously, a reversal of the primary or set up by the products of the volumetric reaction. The duality may of course be disregarded if (1), the secondary reaction is inconsiderable or may be reduced to a negligible quantity, as by high dilution or high concentration of the titrate, addition of the titrand with a certain rapidity, maintaining the titrate at a specific temperature, or the previous incorporation of some product of the primary reaction; (2), the secondary reaction begins or proceeds so slowly that there is no perceptible action during the ordinary period of a titration; (3), the two reactions bear a definite mutual relation and the ratio, found by experiment, can be embodied in the calculation of the result. Otherwise a method based on other than a single reaction is at best doubtful and only suited for approximate determinations.

It does not always follow that a method is disqualified because the reaction involved is somewhat obscure. Many of the volumetric methods in organic analysis are founded on reactions imperfectly understood, yet passable results may be had through standardization by means of a normal sample of the substance under examination with all the conditions identical to those of the analysis, or by a second reverse titration.

2. The titrand to be perfectly stable for at least a few hours, and its strength ascertainable with accuracy by some convenient means.

While every solution should be tested from time to time to guard against a change through evaporation, entrance of dust or fumes, etc., it is nevertheless rather irksome to be obliged to standardize before every titration though only a day or so apart, and therefore the technical chemist chooses where he can a

solution that will remain unchanged for at least several days though it may be somewhat less suitable on other grounds.

The most certain method of standardizing is by means of a freely soluble chemically pure salt that can be readily prepared to correspond to the formula, and offers no difficulties in weighing. If no such compound can be found, a less direct process may answer nearly as well. For titrations where the actual reacting value is of no consequence by reason of the dubious nature of the reactions, the titrand is standardized against the substance to be assayed that may either be of the best obtainable commercial quality or specially purified.

It has been claimed for many crystallized salts chemically pure and neither hygroscopic, efflorescent, or volatile, that simply dissolving an accurately taken weight in water and making up to an accurately measured volume, furnishes at once a standard solution whose titre is as reliable and exact as is given by any other process. No objection can be raised against the principle of this method, and practically it must be conceded that it is hardly logical to make up a solution with great care from a salt of undoubted purity, then proceed to standardize it by a compound of more doubtful composition and under greater probable errors in weighing and solution. On the other hand, by this plan there is no correction provided for the (fairly constant) errors inherent to every titration, which to a greater or less extent are compensated when the titre is established by a titration, under like conditions, of the same or a similar body as that to be determined in practical analysis. Moreover, prudence would seem to point to the desirability of some check on the weighing and measuring of the reagent and solvent, and possible losses or gains in the preparation.

3. Reliable tests for assuring the absence from the titrate of reacting bodies other than the one to be titrated, and if present, methods for their removal and also for other constituents that would interfere by their color, fluorescence, turbidity, obscuration of the end-point, etc.

Volumetric analysis, unlike gravimetric, does not, as a rule, require the separation of other substances accompanying the one to be determined, and in so far is exempt from the inaccuracies attaching to this operation. Yet one should be cautious when dealing with a complex titrate as there may be contained certain bodies that will react with the titrand or interfere with the exhibition of the end-point, and of whose presence there is no indication. Again, a body, in solution or as a finely divided suspended solid, acted on very slowly or practically not at all by the titrand when alone, may be much more readily attacked during the titration of another body associated with it.

The removal of interfering associates in the titrate is usually accomplished by the ordinary methods of gravimetric analysis, selecting such as will leave the titrate free from interfering products of the reactions and employ no reagents whose excess would be detrimental to the titration. If done by precipitation, the scheme of withdrawing for titration a small aliquot part of the supernatant liquid is very suitable as it allows easy duplication.

In some cases a titration is only successful in the presence of a certain extraneous compound in the titrate, that though having no direct action on the titrand, yet causes the volumetric reaction to proceed more rapidly or uniformly, or prevents some secondary reaction. Or the same object may be attained through the introduction of a compound that unites with the titrand in a definite ratio, correcting for the equivalent of titrand by a separate determination.

4. A reasonably wide range through which the rate of titration and condi-

tions of dilution of the titrate, its temperature, degree of acidity or alkalinity, etc., may be varied without detriment to the result.

Certain volumetric reactions proceed normally only in very dilute solutions, while if more concentrated, a reverse or some secondary reaction complicates the principal. On the other hand some titrations are only successful when the titrate is highly concentrated, and although it is a simple matter to dilute a solution, an evaporation means at least the drawback of an expenditure of time.

In the great majority of titration methods the reaction begins promptly and proceeds regularly within the limits of the ordinary temperatures of the laboratory. Exceptions are where the titrate must be kept near or at the boiling point, either because the reaction is only induced or continues normally in a heated solution, or to prevent absorption of carbonic acid from the air, to expel a gaseous product of the reaction, to cause a precipitate to clot and settle, etc. Rarely is the titrate to be maintained at the freezing point of water, this to avoid decomposition of a sensitive organic compound, to retain a volatile constituent, or prevent a secondary reaction.

As a titration proceeds, the concentration of the titrate as regards the active body, proportionally diminishes. In some cases the reaction becomes greatly retarded before the end-point is reached; this difficulty is easiest overcome by a reverse titration.

Under some circumstances a titration proceeds normally only when the titrand is run in very slowly and the titrate so continuously stirred that diffusion takes place immediately; this where a second compound in the titrate reacts like the primary though less promptly, *e. g.*, in titrating an acid by a standard alkali in presence of an easily saponifiable compound. But in general, a practical method will allow the rapidity of titration to be varied within wide limits.

Of the few methods that require a definite ratio of acidity or alkalinity to the volume or concentration of the titrate, none have come into general practical use.

5. A sharp and unmistakeable proof of the consummation of the reaction.

The most satisfactory evidence is a decided change in color of the titrate, although in practiced hands a 'spot' indication is but little inferior except that a somewhat longer time is consumed in a titration. The end-point is shown somewhat earlier or later according to the relative sizes of the drops of indicator and titrate, the time allowed for the color to be developed, the light illuminating the drop, and other variants. Usually these are not sufficient, at least in technical work, to affect the results to any great extent. Less convenient and often less accurate is the indication observed by noting the cessation of precipitation, especially where the precipitate is finely divided and filtered portions must be tested.

In any case, an indication that is not instantaneous, as where the titrate passes insensibly through one color to another and a certain transition shade must be accepted as the end-point, or where the close is marked by the complete solution of a slowly dissolving suspended solid, is always liable to mislead the inexperienced and not infrequently those practiced in the observation.

In the numerous titrations based on a change in valence of an element by the reaction with the titrand, the element may be contained in the body to be examined at the proper valence and not be changed during the process of solution, or if at another valence originally or after solution, can be brought thereto by some simple operation as by boiling or evaporating the solution, or by precipitation and re-solution. More often it is necessary to perduce or re-

duce the element by the action of some reagent. A suitable reagent for the purpose is not always easy to find, since in most cases the excess of the reagent or some product of the reaction will also react with the titrand or the indicator used, and with many reagents it is impossible to remove the excess without again transforming the element; so that one must be selected whose excess can be expelled by boiling or precipitation, or if a solid by solution or filtration.

It is preferred by some chemists to dispense entirely with graduated instruments by weighing a titrand instead of measuring it, the advocates of this system claiming that the time spent at the balance is fully compensated by the greater accuracy of weighing over measuring as ordinarily practiced, the elimination of discrepancies arising from variations in temperature, and minor advantages. On the other hand, the chief attraction of volumetry, for the technical chemist at least, is its rapidity, so that it must be left to each individual operator to decide which plan is best suited to the class of analyses he is called on to perform.

It must be admitted that as a class volumetric methods are inferior in point of accuracy to gravimetric. That an opinion to the contrary is held by many may be explained by the fact that a minority of the methods are capable of furnishing results of unexceptionable exactness when performed with proper care, some even so refined as to be admissible for the determination of atomic weights. The publicity attained by these methods has no doubt created the impression that this standard is reached or approached by most others. Perhaps also the dictum of an eminent chemist to the effect that the highest qualification of a volumetric method is *accuracy*, the next, *accuracy*, and the third, *accuracy* may have had considerable weight, though we are left in doubt as to his reasons for exalting this particular quality — highly desirable of course in any class of methods, it may be and often is sacrificed to other considerations, and in volumetric analysis, peculiarly fitted by rapidity and convenience to the needs of the practical chemist, it would appear that the waiver is the more warrantable. Of the several items that make to impair the accuracy of titration methods, two at least are often in evidence — the sluggishness, incompleteness, or irregularity of the manifestation of the reaction, and the difficulty of expelling or neutralizing the effect of minor reacting or interfering associates, especially when organic, from the titrate.

It is seldom that the determination of all the members of a complex body can be performed by volumetric methods exclusively either as accurately or conveniently as by gravimetric or partly by both. Of the great number of volumetric schemes for the complete analysis of commercial articles and mixtures generally that are to be found in monographs on volumetry, few have come into general practice, and it seems well settled that the field of usefulness for titration methods is largely confined to assays only.

COLORIMETRIC METHODS.

All the various modifications of the practice of colorimetry have as a basis the principle that the depth of color given to a solid or a solution by a chromogenous body is proportional to the weight entering the mixture or dissolved in the solution. From their simplicity and ease of working colorimetric methods are regarded with much favor by technical chemists, but in all cases, uniformity in technic is demanded to a greater extent than in any other class of methods.

Lovibond * summarizes the optical phenomena relating to colorimetric determinations as follows:

* Journ. Socy. Chem. Ind. 1898—206.

"1. Normal white light must be regarded as being made up of the six colour rays — red, orange, yellow, green, blue and violet in equal proportion. When the rays are in unequal proportion the light is abnormal and coloured.

2. The particular colour of an abnormal beam is that of the one preponderating ray if the colour be simple, or of the two preponderating rays if the colour be complex.

3. The rays of a direct light are in a different condition to the same rays after diffusion and give rise to a different set of colour phenomena. (Note — for the present this limits precise colour work to the measurement of diffused daylight.)

4. The vision is not sensitive at the same time to more than two colour rays in the same beam of light; the colours of any other abnormal rays being merged in the general luminosity of the beam.

5. The two colour-rays to which the vision is simultaneously sensitive are always adjacent to each other in the spectrum, red and violet being considered adjacent for this purpose.

6. The vision is unable to appreciate colour in an abnormal beam of light outside certain limits, either

A. Excess of luminosity may mask the colour, or

B. The luminous intensity may be too low for the preponderating rays to excite a definite colour sensation.

7. The length of time required by the vision to appreciate a colour is longest for the red, increasing as the spectrum is ascended, the minimum being in the violet.

8. The colour of a pure substance at a particular density is constant.

9. Every substance has its own specific rate of light absorption, developing definite colour sensations for definite increasing densities."

The essential features of a practical method are

1. The color of the solution of a reasonable weight of the substance to be assayed must be of a depth suitable for a close comparison with the standard.

In practice the best results are secured when a chromogen forms only a small percentage of the substance to be tested; otherwise, since within limits, a nuance is less easily perceived in proportion as the color is deeper, either so small an amount can be dissolved for a test or the solution must be so largely diluted that the errors introduced become excessive and the results only approximate.

For visual reasons some operators will be more successful than others from the ability to more sharply distinguish between closely related depths of a color. Again, a difference in shade of certain colors is more evident to the average eye than of others, a feature familiar to those accustomed to the use of a common form of polariscope.

2. Only the one constituent of the substance assayed to impart a color to the solution. An exception is where the color given by another constituent is so faint that it will entirely or practically vanish on moderate dilution, or may be effaced by some means not interfering with the primary color; or as occasionally happens, where a minor chromogen bears a fairly constant proportion to the substance, the modification of the primary color may be offset by a like addition to the standard, if not already present therein.

A slight extraneous tint from some associate or the solvent itself may be corrected by the interposition of a suitably colored translucent screen, or by viewing the comparison tubes against a tinted reflector.

3. The color not to be transient, at least within the period of comparison. Should the chroma develop as the result of a chemical reaction and not reach

full intensity until after a certain time, then remaining permanent or beginning slowly to lighten, the proper interval between mixing and comparison must be learned by ample experiments.

4. The solutions of the sample and standard to be perfectly clear and free from air-bubbles at the time of comparison, and of a uniform moderate temperature.

A cloud or haze modifies the apparent shade of any color by reason of the opacity of the solid particles, perhaps also by reflection, possibly refraction of light. It is hardly safe to assume that the standard and sample are equally modified when the turbidity appears of the same density in both; the better plan is to fine the solutions by suitable means or to choose a diluent that will act as a solvent.

Many solutions lose their transparency on dilution with water though retaining it when there is substituted alcohol, a dilute acid, etc., according to the nature of the solute and solvent. When a solution through decomposition rapidly clouds and no preservative or retarder can be introduced, it is often possible to so arrange matters that a comparison need occupy but a few moments.

Regarding the influence of temperature, from the results of a large number of experiments on metallic salts made at temperatures ranging from 20° to 60° Cent., Vernon finds that of the three classes, (1), those salts whose solutions increase in color on heating; (2), those which show no change; and (3), those that decrease in color, nearly all of the salts examined belonged to the first class, a few to the second, and none to the third, and that the increments of color on heating show general relations depending on (1), the nature of the base of the salt, ferric solutions being most affected by variations in temperature, next those of cobalt and uranium, then those of copper and nickel; (2), on the nature of the acid radical, chlorides being the most affected, nitrates next, and sulfates least; (3), on the degree of dilution of the solution, sulfates being most affected in their decinormal solutions and least in their centinormal, while chlorides are most affected in their normal solutions and least in their centinormal. He is of the opinion that "the results obtained for the effect of temperature on the colours of salt solutions are without exception, in favour of the hydrate theory of the nature of solution".

5. A comparison standard of accurately known concentration and identical with the assay in color and tone and approximately equal in color-depth.

As the methods of colorimetry are essentially relative, it becomes all-important that there be prepared or selected a suitable standard against which to match the sample. This standard may be

A. The identical element or compound, in a state of known purity, that forms the chromogen of the sample to be tested; as where a nitric acid solution of some copper alloy is matched against a standard of a nitric acid solution of pure copper, or a sulfuric solution of an indigo against one of crystallized indigotin and indirubin. This is the most direct procedure and the one least liable to errors, but for many substances is open to the objection that other constituents of the sample, absent from the standard, may greatly modify the color or depth of the solution.

B. A specimen of the substance to be tested, of superior or average quality, in which the proportion of the chromogen has been determined by an absolute method. The objection to (A) does not apply here, but on the other hand the result is vitiated by whatever inaccuracy attaches to the analysis of the standard.

C. A specimen of the substance to be tested but selected as being of a prime

quality and of undoubted commercial purity — this when the chromogen is of such a nature as not to admit of an absolute determination. The vegetable dye-stuffs are examples. As the selection of the standard is but an arbitrary and personal matter, the results obtained against different standards are hardly comparable, though in technical analysis this difficulty can be overcome by the establishment of an authoritative standard by the co-operation of the trade or industry interested.

D. A more permanent duplicate compounded and hermetically sealed up in a tube of standard diameter — this when the colors of the standards prepared as in (B) and (C) are fugitive, fading by decomposition of the solution either spontaneously, through a reduction by traces of organic matter impossible to exclude, or by exposure to sunlight or air. Usually the foundation is an inorganic salt approaching the desired color, tinged to exact correspondence by other salts.

E. Two solutions of different colors or tints held in glass wedges are superimposed in the path of a ray of white light and adjusted until the transmitted hue matches that from the sample. A serious objection to many applications of this scheme is that variations result from the dissimilar ionic decomposition in the three solutions causing a marked difference in color density. As an example, the color transmitted through two superimposed solutions, one of potassium chromate, the other of chromic acid in molecular ratio to the first, is said to be only about one-fourth as deep as that from a solution of potassium bichromate of equivalent strength ($K_2CrO_4 + H_2CrO_4 = K_2Cr_2O_7 + H_2O$); indicating that with the first two solutions the cathions are K_2 and H_2 and the anion CrO_4, and in the third the cathion is K_2 and the anion Cr_2O_7.

F. A solution, usually of one or more metallic salts, prepared of such a concentration as will permit comparison with all ordinary samples of certain liquids or solutions of certain solids. This conventional form of standard is successfully used for grading complex organic coloring matters. It is clear that no information as to the actual content of the coloring constituent is afforded, but merely an expression of the numerical relation of the respective tints, allowing a more or less arbitrary differentiation; and that the concentration of the standard solution that corresponds to a typical quality of a commercial article or to the maximum color of a food or drink that is compatible with wholesomeness must have been generally accepted by the analytical world ere an expression of this nature can serve a useful purpose.

G. The chromogen of the standard may be developed by the tentative addition of another reagent. For example, a yellow organic solution may be compared against a standard solution of iodine made by running successive small volumes of a standard solution of some oxidizer into a (colorless) solution of potassium iodide; each addition of the former reacts with the potassium iodide to set free an equivalent of iodine which remains in solution. Comparisons of this kind are apt to be tedious, as a certain time must be allowed after each addition of the reagent to insure that the reaction is complete and the color fully developed.

In the comparison of a solution with a standard by the process of tentative dilution it is assumed that the depth of color varies harmoniously with the concentration — in other words, that the shade lightens in direct ratio as the solution is diluted. But experiment shows that this assumption is seldom if ever substantiated, the shade usually lightening, rarely darkening, to a greater extent than is attributable to dilution only.

The reduction in color effect beyond mere dilution is very noticeable in the case of the intensely red ferric sulfocyanide. Magini attributes the hyper-

reduction of color to increasing ionization, but Andrews to hydrolysis (*e. g.*, $Fe_2(CNS)_6 + 6H_2O = Fe_2(OH)_6 + 6HCNS$). Gladstone, from his experiments on the subject, concludes that the amount of ferric sulfocyanide produced on mixing a ferric salt with potassium sulfocyanide is affected by the nature of every substance present, by the mass of the different substances present, and temporarily by variations of temperature, and that in the case of color produced by a chemical reaction, the relative amounts of salts remaining intact depends on their proportion.

Vernon † made an extended investigation in relation to this phenomenon, comparing some 35 solutions of colored salts to learn if dissociation in dilute solutions progressed regularly. An abridged table of his results and a few excerpts from his papers, which should be read in full, are here given.

Dilutions	*1.*	*2.5*	*5.*	*10*	*50*	*100*	*300*	*500*	*700*	*1000*
Copper sulfate	100	....	98.3	95.1	....	93.0	....	....	....	....
Copper acetate	....	100	82.7	68.2	....	37.1	....	....	....	....
Nickel sulfate	100	....	100.1	98.5	86.2	....	...	....	....	....
Cobalt sulfate	100	....	90.8	89.2	....	77.8	....	....	...	....
" " *	....	....	....	100.0	90.0	89.2	83.7	82.0	79.0	77.8
Cobalt chloride	100	....	87.9	76.4	....	65.5	....	....	....	....
Cobalt nitrate	100	....	96.1	89.4	....	79 2	....	....	....	....
Uranium sulfate	....	100	97.1	91.9	....	86.7	....	....	....	....
Chromic sulfate	....	...	....	100.0	94.4	99.8	....	....	....	91.1
" " *	...	....	....	100.0	98.2	97.4	96.2	99.0	104.7	110.2

All the above were diluted suddenly except those marked with an * which were diluted gradually.

"Almost all of the solutions of the 35 coloured salts examined showed considerable decrease in colour effect on dilution, due in all probability to dissociation taking place. The only exceptions are certain chromium derivatives, the colour of whose solutions on gradual dilution, either remains constant or increases slightly. When their solutions are suddenly diluted, different colour values are obtained. Potassium permanganate solution only shows a very slight decrease in colour on dilution. Taken as a whole ferric salts show the greatest decrease in colour effect on dilution of their solutions, then cobalt salts, then uranium salts, and then nickel and cupric salts. Generally also organic salts show the most decrease of colour on dilution, chlorides less, nitrates still less, and sulfates the least . . . . . On comparing solutions of different salts together as to colour effect, it is found that the values obtained bear considerable resemblance to the amounts of decrease of colour the solutions undergo on dilution, organic salts possessing the greatest colour effect, chlorides a lesser effect, sulfates and nitrates a still smaller colour effect."

"From the table [*loc. cit.*] it will be seen that the solutions of the five copper salts examined decrease in colour effect on dilution, the sulfate the least, then the chloride, nitrate, and lastly the acetate which decreases very greatly on dilution. . . . . Nickel salts show much less colour decrease than copper salts, neither the sulfate nor the chloride showing more than a barely appreciable decrease at a dilution of ten litres [a normal solution diluted ten times]. All the cobalt salts dissociate considerably more than the corresponding salts of both nickel and copper; but in this case, though the sulphate is the least dissociable, it is the chloride and not the nitrate that is the most dissociable. The same thing holds for uranyl salts, the sulphate being less dissociable than the nitrate, and this again than the chloride. These salts dis-

† Chem. News, 1892—2—105, 152 and 198.

sociate to a greater extent than copper salts, but not so much as cobalt salts. The acetate of uranium solution however, shows a very different behavior from that of acetate of copper, for it is the least dissociated of any of the uranyl salts examined."

"Chromium salts gave very extraordinary results, for the colour effect of their diluted solutions was found to depend on the method of dilution, according as it was sudden or gradual. . . . . It will be seen that [on gradual dilution] chromic sulfate solution decreases slightly in colour effect till a dilution of 200 litres, but from that point it begins to increase again, till at 1000 litres it is considerably greater than the decinormal solution. . . . . Such extraordinary behavior can only be explained on the supposition that hydrates of different composition and different colour effect are formed, according to the manner of dilution. Iodine dissolved in potassium iodide solution acted in a similar manner to chromic salts. . . . . The results as a whole indicate that dissociation takes place in solutions on the one hand, and hydrates are formed on the other, so it would seem that salts exist in solution in both these conditions at the same time".

"The general conclusions to be drawn from the changes in colour attending the dilution of solutions of coloured salts are, that almost all salt solutions show a decrease in colour effect; but a few, notably several organic salts of iron, show a considerable increase in colour. It is difficult to find an adequate explanation for these changes except on the ground of electrolytic dissociation. . . . . The changes in colour effect of solutions of salts on dilution are evidently due to more than one cause. As will be shown, the formation of hydrates will account for them in part. They cannot be wholly accounted for in this way, however. Electrolytic dissociation seems to be the only ground left on which an explanation is possible".

The practical deductions from the foregoing are that (1), the concentrations of the standard and sample as regards the colorant should be practically identical at the time of final comparison, and (2), that the compositions as regards the other constituents should not greatly differ. The first condition can be nearly enough approached by compounding as indicated by the result of a preliminary test, and the latter by suitable additions to the standard or sample or removal of associates specific to either — this precaution however is in many cases practically unnecessary. It must be remembered that in practical colorimetry the subject is not usually a pure chromogen and hues rather than simple colors are to be compared.

Lovibond* proposes that curves be plotted from the readings of his tintometer for colored liquids at varying concentrations, when it will be found that each liquid will generate a specific curve. In different samples of a commercial article much may be learned from the divergencies of the respective curves as to their relative character and value for a given purpose; thus, the results given by malts in brewing "can be predicted almost with certainty, and this is true of other substances whose curves have been thoroughly worked out". The curves plotting the inharmonious progression of depth and density of solutions of dye-stuffs are said to be characteristic and to serve for distinguishing different dyes.

Unlike volumetric analysis, it would appear that the accuracy of colorimetric determinations is generally underestimated. It is true that the neglect of such precautions as have been pointed out will inevitably vitiate the results, and that certain chromatic bodies are unsuited for comparison by reason of fluores-

* Journ. Socy. Chem. Ind. 1896—207.

cence or dichroism, yet as technical methods go, under reasonable conditions and care, the results are quite exact enough for practical ends. The limits of accuracy under favorable conditions have been variously stated as "an average of one per cent", "two per cent or less", and by a less conservative writer "as close . . . . . as one-tenth of one per cent". In assigning limits it must of course be taken into consideration that in comparison of colors no two visions are of exactly the same acuteness; still there are comparatively few who cannot distinguish fairly closely related depths or shades of a color.

In consequence of the highly tinctorial qualities of many bodies, either inherent or that can be generated or enhanced by some chemical transformation, colorimetric methods can often be applied to smaller weights than could possibly suffice for methods of other kinds. It is also well adapted to the determination of small proportions of colorific metals, as a suitable standard is easily prepared from the pure metal or one of its definite compounds.

ATTRIBUTIVE METHODS.

Frequently in technical and sometimes in scientific analysis, one meets with mixtures where an actual separation of the constituents is difficult or impossible by any known means, and recourse is had to methods based on the determination of some physical or chemical constant of the mixture, the resultant of a differential common constant of the constituents. And outside of the many instances where it is his sole recourse, in many cases the scheme is so profitable in point of time, labor or attention, that the chemist will adopt it in preference to a direct method.

From the similarity of the calculations involved, methods based on the determination of a common constituent of two admixed bodies are included under attributive methods in Chapter 7.

For practical purposes mixtures of two or three analogous bodies may be divided into three classes: (1), those where the constant of any mixture varies directly with the proportions of the constituents; in other words, that the curve whose ordinates represent units of the constant, and abscissae the relative percentages of the constituents of the mixture is a straight line or practically so; (2), where from inter-reaction, the constants of the mixtures do not vary directly with the ratios of the constituents; and (3), where for a limited space the curve of (2) is practically a straight line.

The laws governing the inter-reaction of mixtures are but imperfectly understood and as we cannot confidently forecast into which of the above classes a given mixture will fall, direct experiment must be resorted to for positive information. In (2) and (3) the curve is distinctive for each binary mixture and is only to be plotted from sufficiently extended data.

In complex mixtures there is often some uncertainty as to whether the resultant of the constants of two bodies is not modified by the presence of some associate in the mixture. This interference has sometimes been confounded with an inter-reaction of the active bodies themselves, the correct reason appearing only on examination of carefully prepared pure mixtures.

The general formula (page 155) for a binary mixture is $X = 100\frac{d-b}{a-b}$, where X is the percentage of one constituent; a and b the constants of the constituents, and d, the constant of the mixture. On the presumption that the three values can be determined with absolute accuracy, it is immaterial how little a and b differ. But as there is always some, and frequently a considerable inaccuracy, the more divergent these values the less is X affected by an error on

any of the three; thus, the lesser value b being constant, d increases in proportion with a, and the numerical values of the terms of the fraction $\frac{d}{a}$ become correspondingly greater in relation to $\frac{b}{b}$; hence an equal error in the determination of d is of less importance.

In class (2) experiments determining the amount of divergence of d from the calculated values will decide to what extent interpolation can be carried compatible with fair results. Where a and b differ considerably, at a certain range in the proportions of a mixture the consecutive values of d may differ so slightly that no confidence can be placed in the results. This range may be but small, or may cover nearly all percentages of one constituent. Usually the curve of the constants traced by consecutive proportions of the constituents becomes far more abrupt near one or both ends, though the reverse is sometimes true.

Errors in fixing the constants, outside of the ordinary analytical deviations, may arise from the difficulty of obtaining the two constituents in a pure state, or from the variance due to their being (1), of different origin or changed by age, mode of preservation, degree of refinement, etc.; (2), both members of a group of allied bodies that possess certain common characteristics complicating the determinations; or (3), each constituent itself a complex mixture of somewhat indefinite composition, where the constants may on the one hand be confined to quite narrow limits, the mean of the individual members, or on the other hand the variations be so great as to make an attributive method valueless. In dealing with any of the above the chemist will be prudent if he personally determines the constants of a and b under the same conditions and upon the same materials (as far as possible) that form the mixture in question, rather than depend upon the data of others. In natural products where the value of a or b is subject to large variations, it is also important that the chemist learn whether the sample is a mixture of but two individual bodies, or if one constituent, or both, is itself a composite, in the latter case accepting only the mean of several concordant determinations made on different parts of the sample.

The identity of an unknown compound or mixture that may be any one of a group or class of allied bodies may be inferred from a comparison of the constants with tables compiled from previous observations for members of that class (page 156.) A deduction is the more dependable (1), the less complex is the body in question and the less its properties are dependent on the past history of the body; (2), the greater the number of different constants that can be determined and compared, and their reasonably close agreement with established data; (3), the more nearly the material operated on and the details of the determinations approach those of the compilers of the tables of constants.

As a class, attributive methods afford reliable and fairly accurate results on mixtures of two active bodies alone or on one or two active bodies in presence of others that have an absolute or practical zero-value for the selected property. Theoretically the proportions of a mixture of n bodies can be calculated from $n - 1$ properties, but practically no higher than a ternary mixture is attempted on account of the great number of determinations required for the calculations with the liability of some one or more being incorrect; moreover for a given material there can but rarely be found more than two properties whose constants are at once sufficiently divergent and exactly measureable.

An advantage over other classes of methods is that in most physical methods

but a comparatively small amount of material is needed for a determination and that it remains intact and available for further tests, a feature appreciated where the supply of material furnished the chemist is limited by reason of its rarity or high cost; also where the integrity of the material in its original form is not to be disturbed or where it cannot be removed from an established locality — here certain physical methods (*e. g.*, electrical conductivity) can sometimes be applied. But unless the material is known to be homogeneous one must guard against an illusive conclusion by making several determinations on different parts of the material.

Of the errors that may be incurred during an analysis some are observed at once, others may pass unnoticed should the attention of the operator be diverted for the moment, and can only be located, if at all, by some palpably erroneous result manifest after the analysis is finished. It is within the experience of every chemist that at times the result of an analysis is unaccountably so far from what was expected that he is puzzled to account for the cause, unaware of any slip on his part that could explain the failure.

Both personal errors and those inherent to the method may be such that a loss during one operation will be measureably compensated by a gain in another and the final result be not greatly vitiated; but it is more usual that they tend in the same direction and are cumulative. And it must be remembered that the effect of a loss or gain in any one operation may not be confined to the result on a single constituent but extend to subsequent determinations as well.

The operative errors have been discussed in Chap. 9; let us consider those arising from other sources.

1. The material for analysis may be of a composition not covered by the method. The percentage of the constituent determined may be greater or less than was contemplated by the deviser; some exceptionally-occurring interfering body may be contained, or one absent that is essential; again, the physical properties of some one of a class of bodies may so largely differ from others as to exclude methods dependent to any degree on the constancy of the physical condition of the substance.

Many methods of quantitative analysis are adaptations of qualitative tests. Where the presence of an element is manifested by the formation of a precipitate with a particular reagent it may be presumed that the reaction can be applied for the determination and perhaps the separation of the element; or an exact reaction may be made the basis of a volumetric assay. Yet there are many reactions unsuited to this conversion, disqualified by reasons of less or no consequence in qualitative analysis; thus, indefinite composition of a precipitate, incomplete insolubility, a state of agglomeration opposing easy filtration and washing, alteration on heating; in colorimetry, a color developed that is transient or unsuited for comparison; etc.

A quantitative should be preceded by a complete qualitative analysis that one may proceed with the separations and determinations in a methodical way; in many cases it is imperative for assurance of the absence of whatever might interfere with the course reactions. Under certain circumstances, however, a qualitative examination can be abridged or entirely omitted; thus

A. The composition or nature of the commonly occurring impurities may be known as nearly as need be from the origin or nature of the substance, as in minerals, commercial salts, alloys, drugs. The habitus or physical characteristics — color, taste, transparency, fluidity, odor, peculiarities of aggregation,

etc., may indicate certain associates or exclude those but occasionally met with. In proportion as one becomes conversant with chemical technology can he pronounce with confidence on the nature and composition of a complex commercial body, and in doubtful cases decide from a few special tests what otherwise could only be learned from a systematic examination.

B. The composition of an artificial mixture may be inferred from the constitution of other articles employed for the same or a similar purpose; many classes of commercial articles designed for special applications are characterized by a general similarity in composition.

The limit of the cost of production or manufacture of a commercial article as fixed by competition forbids the admission of the more expensive ingredients or those that entail manipulations of an extensive or unusual kind. And adulteration or an inferior or debased quality is to be suspected when an article is offered at a price considerably below that ruling on the open market. Practically, adulteration is only practiced where the cost of production can be so far reduced that the profit is a sufficient inducement to risk detection and exposure, except cases where the difficulty of distinguishing the adulterant from the genuine makes sophistication a comparatively safe proceeding.

C. The substance may have been subjected to some physical or chemical treatment — *e. g.*, evaporation, fusing, washing, sublimation, aeration — that would perforce have removed certain bodies had they been originally present. Again, that a certain compound is contained in a mixture may be prima facie evidence against the co-existence of certain other bodies that would act chemically or mechanically on the former, or modify some of its manifest qualities; per contra, there may be implied or suggested an associate essential to the integrity of the first or conferring or enhancing some particular property, or as a coadjuvant. How often are these truisms overlooked!

D. Some simple preliminary operation may reveal the constitution as nearly as need be. Thus, the mixture may be treated with a diluent or a selective solvent to take up some constituent that by its mass, opacity, or intense color obscures its associates. If the constitution of the residue cannot be easily recognized on inspection by the shape, color, or other peculiarities of the particles, it may be examined under the microscope, separated into layers by agitation with water, or otherwise.

E. In an assay a specific reagent or some physical process may be applied that will affect only the body it is desired to determine, or perhaps a few others also that may afterward be looked for and separated; or a certain operation may withdraw all or nearly all of the other constituents of the mixture.

But in drawing a conclusion from any of the above, due caution will often save time and trouble, for it is well to recognize the possibility of the presence of what is least suspected.

2. The method, designed only for rapid approximate work, may fail where greater accuracy is essential. The temptation to adopt such methods for important determinations is greatest in industrial analysis where the chemist is often burdened with more than he can properly attend to in the limited time allowed, but while the task may be lightened thereby, the substitution is always attended with hazard and may at any time prove a source of anxiety, perhaps humiliation.

3. The tables of the atomic weights of the elements are periodically revised to conform with later and presumably more reliable data. With each revision the values assigned to some of the elements are more or less altered — the common elements but slightly if at all — and an analysis calculated accord-

ing to the figures of different tables may show somewhat different results. In a few instances, calculations from the most divergent of the figures on one or more elements may show considerable variations.* But generally the difference is of less moment than might be supposed, for as the determination of an atomic weight follows the lines of a quantitative analysis, whenever there is available for an element a method of analysis so exact that the result would be vitiated by a slight change in the atomic weights concerned in the calculations, it will be found that a correspondingly exact process has been used for the determination of the latter, and the more recent values are almost identical. Conversely, when recent values for any element markedly differ, the inference is that no exact methods are known for the analysis of bodies containing it. However, it is always the best plan to compute according to the latest authorized data.

4. Exceptionally a determination may be complicated by certain abnormal manifestations, phenomena apparently at variance with chemical laws, or by some irregular or capricious deportment manifest under ordinary working conditions.

It is well known that under certain conditions confined within narrow limits issue precipitates of anomalous composition or aggregation or segregating more slowly than is usual; that in a solution there may exist between two elements a state of libration immediately overset by the introduction of a minute excess of either, or a reaction-lag terminated by the addition of a trace of one of the products; that reactions commonly expressed by a single equation are not exhibited as an instantaneous transposition but as several fractions or installments, a major preceded or followed by one or several minor; and that the normal conduct of a reaction may be profoundly modified by the presence of an apparently inconsiderable amount of a foreign body unconnected with the reaction.

In organic analyses there must be recognized the influence of some preliminary treatment, mode of extraction of a constituent, age, etc., to hinder complete precipitation or prevent it entirely; and it must be remembered that these influences, of the greatest importance in the determination, may not be manifested to such an extent as to prevent recognition of the body in the previous qualitative examination.

The physical constants of certain bodies may be largely altered by a temporary change in the molecular arrangement, not returning to the normal for many hours or even days. Certain combinations of a metal with animal matter, induced by passing through the living body or by close contact with the tissues immediately after death, exhibit abnormal reactions, and it is said that the chemical activity of proteids of certain living animal matter is far more intense than when derived from the cadaver.

The mutual action of certain admixed bodies to lessen the respective solubility or insolubility in a solvent is well known. Thus, in the separation of the rare earths, some are insoluble in a solution of potassium sulfate, others freely soluble, but when members of each class are in admixture the sharp line of demarcation is suppressed, some minor form of adhesion appears, and only imperfect results can be had in one operation. Zirconia and titanic acid considerably modify the reactions of each other, as do ruthenium and iridium; in a mixture of the two alkaloids, quinine is less and cinchonidine more soluble in ether than when alone. Paraffin (*parum-affinis*), so indifferent to reagents even when highly subdivided, is noticeably acted on when diluted with bees-wax.

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* Chem. News, 1896—2—143; Crookes Select Methods, 16.

The same effect may be noted where the process of solution involves a manifest reaction; platinum is insoluble in nitric acid, yet when alloyed with a large proportion of silver both dissolve readily and completely; the conversion of strontium sulfate to carbonate is prompt and thorough when alone, but less so if in admixture with barium sulfate, while at the same time the latter body is acted on to some extent; etc.

And generally, there must be recognized the influence of associated bodies and their derivatives to modify the chemical activity of reacting elements and disturb the normal exhibition of the reactions, even to induce a reaction the reverse of the normal, as an oxidation instead of a reduction.

Phenomena such as mentioned above are so striking as to challenge the notice of even the most inattentive, yet who can say where may not exist the same or like influences effective to a lesser degree, unnoticeable though not to be ignored, and perhaps where least expected? It is more than possible that many of the irregular manifestations that at one time or another perplex every analyst can be charged, in part at least, to influences like these whose exhibition ordinarily is minimized or suppressed by unfavorable conditions, and be readily explainable were the extent of the influences and the conditions favoring their assertion but known. Even in the extreme case of a synthetic proof, though so compounded as to differ but little from its natural prototype, may yet be affected by the unavoidable variation in composition to a degree greater than the total of the errors it is intended to measure.

In any event, the wisdom of proceeding cautiously when dealing with unfamiliar material is apparent.

5. In this connection may be considered the personal equation of the chemist, his interpretation of general directions, or certain peculiarities of manipulation that have become habitual. Though in the main of small import, they may at times seriously affect the outcome of an analysis; for example, an unqualified direction to concentrate a liquid by evaporation would be understood by some to allow a brisk boiling down, while others would restrict the heat to that of the water bath, with not infrequently a marked difference in the composition of the resulting syrup; the same is true of many other operations.

It is frequently remarked that a chemist will hold to methods regarded by most as antiquated and inferior to those in more general use. That they are equally successful in his hands can be attributed to certain peculiarities of manipulation or a close attention to details apparently so insignificant as to be overlooked by others, but of whose importance he is aware through long experience. Doubtless conservatism may be carried to an extreme in some cases, nevertheless it is soon learned that in analysis as elsewhere, novelty does not always imply superiority.

The question may arise as to how far it is advisable for the beginner to conform his modes of manipulation to the directions of a text-book or to imitate the practice of one more experienced. That a chemist of undoubted skill performs a certain operation of the routine of analysis in a particular way, insists on the adoption of seemingly unimportant precautions, or does not hesitate to neglect measures that are commonly believed the part of prudence and without apparent detriment to the correctness of his work, does not imply that the more usual practices should be renounced, but rather illustrates the flexibility of analytical practice in general, the possibility of a wide variance in details compatible with satisfactory results. And while the student must perforce follow the standard practice to a great extent he should nevertheless endeavor to individualize his work as far as may be, always with the view of reducing mechanical or other errors to a minimum. Of course where

specific directions are laid down in a scheme of analysis it is presumed that the author had good reasons for their interjection and it is well to follow them without deviation—at least when it is not considered worth the while to investigate as to their necessity.

6. Finally, the method itself may be at fault, and this more often than would be expected.

As regards the quality of accuracy it may be said that the capabilities of the ordinary methods are more apt to be overestimated than underestimated. For it must be remembered that a new method is judged mainly by the test analyses appended to the description of the method. These analyses, intended to support the claim of the method to consideration, are always made under the most advantageous auspices in all respects; yet too often only the most favorable of the results obtained appear, not that the suppression of those less flattering was done to conceal the shortcomings of the method, but rather from the natural proneness of the inventor to discover some flaw in manipulation or elsewhere sufficient to warrant their omission. Later, the few who are in a position to critically examine the method and compare it with others may not feel called on to express their conclusions regarding it, or if so, their criticisms may not obtain the publicity accorded the original description.

Usually a method for the analysis of an inorganic body or a substance of commercial value will sooner or later be judged on its merits alone and take its place among those having the confidence of analysts in general, or join the vast array of the doubtful or condemned. Less readily classified are those which measure not a stable, active, definite compound or element but some indefinite, complex, or ill-understood principle, methods without pretensions of determining a single chemical compound, but the results expressing only the relative value of the substance analyzed — one of this class is often the subject of extended and perhaps acrimonious controversy.

Again, a technical method may be unsuited to the material in hand, it having been designed to cover only a special substance or class of substances of which an analysis is less frequently called for either on account of a limited use in the arts or that the constituent proposed to be determined has but a small influence on the physical properties or commercial value of the substance containing it, and although excellent from every point of view, the method does not attain the publicity reached by those of a broader scope and therefore is less likely to attract the attention of those who would modify it to answer for other and more general purposes.

Of the defects sufficient to condemn a method for practical use, perhaps the most common can be charged to the fact that the originator, fearful as to his title to priority, has hastened to announce his invention before an exhaustive examination has confirmed its worth, claiming general applicability from results on but a special class of bodies; assuming that, with a few modifications, a method known to be qualified for the analysis of one substance will be equally suitable for a similar one, and taking no cognizance of the effect of associated constituents. To what extent an associate may exert an influence on the reactions of others has already been stated.

In other instances the deviser has apparently assumed that methods will always admit of reversal, the reagent becoming the compound determined, or that specific methods of determination can invariably be applied for separation, and has considered a practical trial superfluous. Absurdities are often the issue of this expedient of writing-desk invention; as an example may be cited the directions formerly laid down by a standard work on pharmaceutical

practice for determining the purity of commercial oxalic acid by titration with standard potassium permanganate, while under the directions for standardizing the latter, advised the use of commercial oxalic acid! Such an oversight could hardly have remained undetected had but a single trial been made. Certainly what is worth publishing is worth at least one confirmation.

Again, variations in the physical structure of a body may greatly modify its solubility or decomposibility, certain specimens yielding readily to a solvent or flux, others resisting prolonged treatment, and it cannot be doubted that many schemes advised for the resolution of a refractory body (chromite, for example) have been tried only on one of the more easily decomposed varieties.

The sample originally tested, if a natural product, may have been freshly gathered and analyzed near the place of its growth, or if a manufactured article, tested immediately following production; other samples reaching a chemist may have been altered by age, exposure, or internal reactions, and if analyzed by the same method, that may be chemical or physical, do not furnish equally satisfactory results. And if the proportion of the leading constituent of a substance is arrived at by a computation from the proportion of some constant associate, it is often doubtful whether the latter may not have been profoundly altered by the influences mentioned above or by others equally potent.

Or granted that the method is correct in theory and practically serviceable, the published description may be anything but lucid. Details that might safely be left to the discretion of the chemist are iterated to the extent of confusing and distracting his attention from the more vital points that are consequently overlooked. The importance of clearness and brevity in this regard is brought home most forcibly to whoever has occasion to search through many volumes of a journal — perhaps in an unfamiliar tongue — for information on a subject not appearing in their indices. It is certainly depressing to read through pages of closely printed matter to find at last that the prolix whole but describes a trifling modification of dubious worth that might well have been compressed to the compass of a single paragraph.

Or the fault may lie in the other extreme; the fundamental principles may not be elucidated with sufficient clearness — often they are omitted entirely, the writer evidently taking it for granted that the reader is so familiar with the subject that their incorporation would be superfluous, forgetting that a thorough knowledge of one specialty in addition to a general acquaintance with other departments is all that can be expected of the average analyst; or some important details may have been omitted or passed over with a bare mention. Where brevity necessitates ambiguity or the omission of essential information we can well tolerate a more diffuse style — even "the almost epic breadth in which our continental brethren indulge".

The absolute or relative accuracy of a method for the determination of a constituent of a given material may be tested in several ways.

1. For a method designed for the determination of the constituents of a chemical compound, the agreement of the results with the percentages calculated from the formula of the compound is a measure of the correctness of the method as practiced under the degree of skill and experience possessed by the operator.

2. By synthesis. A known weight of the pure constituent to be determined is compounded with such others as are contained in the substance analyzed in approximately the same proportions, and an analysis made on the mixture by

the method to be tested. This scheme is the most unequivocal of any except that of (1), but unfortunately cannot be availed in all cases, for not only must the actual proximate composition be known with certainty, but it is often impossible to reproduce the peculiar combinations and physical conditions of the original. As to what extent this is essential for the purpose in any given case must be left to the discretion of the chemist.

Sometimes the constituent to be determined can be wholly extracted from the substance without material alteration of the remainder, after which a known weight of the pure constituent may be added and the analysis proceeded with.

A plan frequently adopted is to make two determinations, one on the substance itself, the other after the addition of a known weight of the pure constituent. The difference between the two results will approach the added weight in proportion to the accuracy of the method.

3. The most usual method is that of comparison of the results afforded on a given sample by the method in question with those by another differing in principle or at least in conduct, and of good repute as to accuracy and reliability. The conclusions are the more convincing where the means of the constant errors of the two methods tend in opposite directions.

4. In a gravimetric analysis the final product as weighed is again put through the same operations as in the analysis, then reweighed, the loss or gain presumed to be in a measure equal to that incurred in the original analysis. But here the modifying effect of the associates found in the original sample is absent, an omission that may sometimes vitiate the result to a greater extent than the inherent errors of the method itself.

5. Through uniformity of manipulation and details in the conduct of duplicate analyses, even a highly defective method may give results that agree closely though both far from the truth. But if unequal (and preferably greatly differing) weights of the sample are taken for the determination and the details varied where the largest errors are supposed to lie, a fair idea of the standing of the method can be argued in most cases.

6. In default of any direct means of comparison, the method may be scrutinized in the light of experience with other methods similar in character, noting where errors are most likely to occur and their probable magnitude. It may be possible to prove by a few experiments that the errors are inconsequential, or, taking into consideration the nature of the substance in hand and the degree of accuracy attainable by other methods, that they can be neglected. On the other hand, their gravity may be so apparent as to discredit the method, at least for more than approximations.

It does not always follow that the directions formulated in the description of a method are best suited to a particular analysis. Although for many bodies we have as yet only arbitrary codes that are to be followed literally, yet the majority of methods will allow some and often a great variation in technic without lessening their accuracy; and the more generally applicable a method, the greater the probability that it can be modified with advantage for a given determination.

When one would essay the emendation of the details of a method he should bear in mind two matters of importance, first, that one particular flaw may be so significant as to make useless any effort to improve other particulars while it remains, and even when the method is free from any one pronounced defect, nevertheless there is always some weakest link, some detail wherein lies the

greatest imperfection or liability to error, and to this should his attention be first directed; second, that a change apparently advantageous, may originate a defect of a different nature greater than the one sought to be rectified. Yet often are such obvious cautions neglected.

And in the application of analytical methods, along the line of theoretical correctness there is a point where practicability ends, a limit specific to the method and the individual, and so important is the ability to recognize this boundary between the possible and the feasible that it may justly be deemed the highest accomplishment of the practical analyst.

The errors inherent to a method may to some degree be guarded against or corrected for as follows.

1. All unnecessary operations should be omitted. Thus, by a little foresight or care the bulk of a solution may be kept so small that an evaporation can often be dispensed with or deferred to near the close of the analysis, and the losses or gains incurred in this operation concentrated on one constituent, perhaps one less important than others, instead of being distributed among several; by combining two precipitations, one filtration may be dispensed with; etc.

It is not uncommon that the specific directions enumerated as being essential to the successful conduct of a method are in reality but a record of those employed in the few experiments made to substantiate the claims of the author. Handed down from one text-book to another, they are regarded as part and parcel of the method until finally shown by some skeptical investigator to be of no special importance and often to be changed with advantage.

2. Certain manipulations in the course of analysis can hardly be performed without some mechanical loss unless great care is exercised, and in so far detract from any method that may direct them; such are the trituration of a powder in a mortar alone or with a liquid and transference to and fro; mixing powders by grinding; the mechanical removal of a precipitate from a filter; elutriation; deflagration; etc. Though sometimes unavoidable, it is well to seek whether some less hazardous process will not accomplish the same purpose, for one of these may have been specified simply for the reason that the deviser was familiar with it through practice in some branch of practical chemistry or pharmacy where the operation is of frequent occurrence.

3. With equal errors in manipulation, the results by a given method are accurate in proportion to the amount of material operated on, and frequently the weight directed by a method may be materially increased with advantage. In certain cases however there are valid reasons for taking a comparatively small weight; as where the supply of material is limited or very costly; with materials dangerous, as high explosives, or offensive; where a tedious preparation, as exceptionally fine grinding, is needed; or where solutions must be very highly diluted, or bulky precipitates are formed.

4. A modification of the routine for the separation of the constituents of a complex mixture may give more accurate results than where the usual sequence is followed. Conditions that will decide whether the order should be changed are the relative weights of the constituents, their relative importance for practical purposes, the difficulty or inconvenience of separating any two, the accuracy required, etc. Similar considerations will decide whether a given constituent is best determined as separated in the regular course of analysis or by specific treatment of a separate portion of the original material.

5. Some of the factors tending to magnify a result may be allowed for by running a blank determination along with the analysis, identical with it in every way except in the omission of the substance analyzed. At first sight this would

seem to offer a means of correction comprehensive and exact, yet its utility is more apparent than real, since it does not as a rule cover the faults common to most analyses. Moreover the absence of the substance to be analyzed is *per se* capable of altering the conditions of the analysis; for example, a flocculent precipitate will mechanically carry down and retain colloidal matter which in a blank determination would remain suspended in the solution.

A parallel or control determination or essayette is far better adapted to the purpose, especially in organic assaying, though even in a synthetic proof a difference in deportment may be shown, due to an imperfect admixture of the constituents as compared with the natural substance, one prepared by precipitation, etc.

6. The result of a determination may legitimately be altered for only those errors whose nature and extent are definitely known or for which the proper allowance has been previously ascertained. In general, a method that requires the result to be empirically corrected may be considered in so far defective.

The correction for a loss or gain in a determination may be ascertained from (1), theoretical deductions; (2), data secured by a subsequent operation either of the regular course of analysis or a special test; (3), the loss or gain sustained by a synthetic proof or a known weight of the pure compound, when submitted to the regular analysis; (4), the loss or gain sustained when a weighed precipitate is put through the same process as the original sample; (5), the deviation of the result on an average sample of the substance from that afforded on the same sample when analyzed by another method. Of the above, only the first, depending on stoichiometrical laws, can be considered unexceptionable as not being subject to variation through the personal equation. Should the correction be in the shape of an addition or deduction of a fixed quantity, the technic must be prosecuted under at least fairly corresponding conditions to those employed in ascertaining the correction.

The correction is usually applied numerically at the time of calculation of the results, adding or deducting the quantity calculated or otherwise ascertained to the weight of a precipitate or residue or the volume of a liquid or gas. In a few methods there is added while the analysis is in progress a weighed amount of the constituent determined or of some analogous body to lessen or counteract a specific effect of an interfering constituent, or more rarely, to increase its potency up to a known or measurable extent.

In gravimetric analysis the most common corrections are the deductions for the weight of the ash of filter paper and impurities in reagents, and additions for losses due to solubility and by volatilization on evaporation of solutions or ignition of precipitates; in volumetric analysis for the temperature of standard solutions, the excess of titrand to show the end-point, and for the space occupied by a precipitate or residue in a liquid to be divided; in gasometry, for aqueous vapor in a gas; in colorimetry, for the effect of a minor colorant; and in physical determinations, for the usual experimental variances.

A correction for the incomplete insolubility of a precipitate in an aqueous solution based on its coefficient of solubility in water is not to be depended on since the solubility is sometimes lessened, sometimes increased, by the excess of the precipitant or other dissolved compounds; similarly, the rate of solubility of a gas in a liquid is modified by the dissolved matter of the latter as also by the duration and closeness of their contact and the presence of another dissolved gas. Where the solubility of a precipitate is too great to be neglected, the loss is found from a parallel determination on the pure constituent under conditions as nearly identical with the analysis as possible; this where

the better plan of previously saturating the liquid with the same compound as the precipitate at the temperature of the analysis cannot be availed.

Before attempting an analysis by a method with which he is unacquainted, the student should first study the principles until clearly understood, then critically examine the details, endeavoring to determine the nature of the errors likely to be encountered and how far they will severally and conjointly affect the result; whether any two act in opposite directions and tend to offset each other, or those likely to prove serious may not be eluded by modification or suppression of certain operations; if the quantity of sample directed is sufficiently large for the degree of accuracy required yet not too great for convenience and reasonable speed; and, should any special weights of reagents be advised, that they are adequate but not unreasonably excessive and not mis-stated through typographical errors; etc.

As an example let us scrutinize the details formulated for the exercise on page 245, the determination of nitrogen in ammonium sulfate. A weight of .200 gram of pure ammonium sulfate is decomposed in a nitrometer by a solution of 10 grams of sodium hydrate and 2.5 Cc. of bromine. Nitrogen is formed by the decomposition of the salt —

$6NaOH + 6Br = 3NaOBr + 3NaBr + 3H_2O$; and

$(NH_4)_2SO_4 + 2NaOH + 3NaOBr = N_2 + 3NaBr + Na_2SO_4 + 5H_2O$,

and is measured over water and the weight of nitrogen calculated from its volume by the equation

$N = (V + .5) \times (B - F) \times \frac{.0012652}{760\,(1 + .00367t)} \times \frac{100}{S}$; where N is the percentage of nitrogen in the salt; V, the observed volume of gas; .5 Cc., the correction for the absorption of nitrogen in the liquid; B, the height of the barometer in millimeters; F, the tension of aqueous vapor at the observed temperature; t, the temperature of the room in degrees Cent.; and S, the weight of the sample.

1. Will the weight of .200 gram of ammonium sulfate liberate a volume of nitrogen suitable for measurement in a burette of 50 Cc. capacity, even at the extremes of high temperature and low pressure — say 30° Cent. and 700 Mm. of mercury — to be met with in practice?

Since $(NH_4)_2SO_4$ (132.214) liberates N_2 (28.08) we calculate that .200 gram of the salt evolves .042477 gram of nitrogen, and, as one cubic centimeter of nitrogen weighs .0012562 gram under normal conditions, a volume of 33.81 Cc. This corresponds to a volume of 42.68 Cc. measured moist at 30° Cent. and at 700 Mm.

2. Are the proportions of the reagents as stated sufficient for the weight of ammonium sulfate directed?

Uniting the equations given we have

$$\underset{132.214}{(NH_4)_2SO_4} + \underset{479.7}{6Br} + \underset{320.464}{8NaOH} = \underset{28.08}{N_2} + 6NaBr + Na_2SO_4 + 8H_2O.$$

From the above equation it can be calculated that .200 gram of the salt is decomposed by .726 gram of bromine with .485 gram of sodium hydrate; as there are directed fully ten times these weights the necessary excess is amply provided for.

We may now estimate the effect of

1. Impurities or moisture in the ammonium sulfate.

Simply that for every milligram of impurity in the .200 gram, the percentage

of nitrogen is reduced by .005 of 21.24 per cent (the theoretical yield) equal to .11 per cent—this on the supposition that the impurity is such that no nitrogen is evolved from it by sodium hypobromite, for were it another salt of ammonium, as the chloride or nitrate the percentage of nitrogen would be increased instead of diminished.

2. An incorrect weight due to a defective balance or weights, or an error in casting up the weights.

Similarly, each milligram over or under the true weight raises or lowers the nitrogen by .11 per cent.

3. Defective calibration of the thermometer or a misreading.

From the equations *ante* it may be calculated that the theoretical yield of gas from .200 gram of the salt measures 37.14 Cc., at a temperature of 20° and a pressure of 760 Mm. and saturated with water vapor, and at 21° the volume would be 37.33 Cc. Here the difference corresponding to one degree is .19 Cc. Since one Cc. of nitrogen under normal conditions corresponds to .63 per cent nitrogen in .200 gram, then .19 Cc. equals .12 per cent, the error incurred by a deviation of one degree Cent.

4. A change in temperature between the two readings of the thermometer.

Here the apparatus may be likened to an air-thermometer; if the volume of gases in the bottle, burette and connecting tube is say 100 Cc. at 20° and 760 Mm. moist, the expansion for one degree is .50 Cc., and since there is a difference of one per cent in the result for a variation of 1.75 Cc. under these conditions, each degree of rise or fall in the interval between the readings makes a difference of about .29 per cent in the result; the expansion of the solution for one degree is about .02 Cc. per 100 Cc., compensated in a measure by the expansion of the glass.

5. Defective calibration of the barometer or a mistake in reading it.

As in (3), 37.14 Cc. of moist nitrogen at 20° and 760 Mm. equals 21.24 per cent of nitrogen in the ammonium sulfate; if the pressure should be incorrectly observed as 761 Mm., the calculated percentage would be 21.27, a difference of .03 per cent for one millimeter.

6. A change in atmospheric pressure in the interval between the two readings of the barometer.

As in (4), taking the volume of the gases to be 100 Cc. at 20° and 760 Mm. moist, an increase in pressure to 761 Mm. would diminish the volume to 99.87 Cc., a difference of .13 Cc. This corresponds to about .08 per cent of nitrogen for each milimeter of mercury.

7. Absorption of nitrogen by water in the burette.

The trapping water measures say 100 Cc., and as the coefficient of absorption for nitrogen at 20° is .014031, were the water air-free only 1.4 Cc. could possibly be absorbed. As the water is largely saturated with air, the surface exposed to the gases but small, and the time of contact limited, only a fraction of this volume can be taken up.

8. Retention of nitrogen in the generating fluid.

The correction based on direct experiment is .5 Cc., which is about the same volume as would be absorbed were the liquid water and the gas pure nitrogen. It is probable that the volume named is correct within ± .1 Cc.

We may conclude from this data that the source of the largest error is likely to be a variation of the temperature of the room wherein the analysis is done, and hence great care should be exercised against draughts, currents of hot air from burners, heat radiated from the body, etc. If there is a change, notwithstanding these precautions, the approximate volumes of the air and air plus nitrogen may be found and both readings reduced to the normal. It follows

that the smaller the volume of the gases the less will the reading be altered by a given variation in temperature, hence the bottle and the upper ungraduated part of the burette should be as small as practicable.

Usually the barometer will not rise or fall appreciably during a test; if so, the effect of the difference may be eliminated by the reduction as stated above.

As the salt is readily purified and not hygroscopic, the errors of (1) and (2) need only be referred to in the way of a caution, and with reasonable care will never be incurred. The figures of (3) and (5) point to the necessity of knowing by actual test or comparison with normal instruments that the thermometer and barometer are correctly calibrated.

Following the general rule, the accuracy of the determination is increased by a larger weight of sample with a proportionally larger burette.

On the same lines as the above should all gravimetric or other methods be examined; the items to be scrutinized will readily suggest themselves to the student. It must be observed however that whenever more than one element or compound is to be determined in the same weighed portion of a sample, certain errors may entail to the determinations following the one in question.

In an analysis of a chemical compound of known purity the approximation of the percentage of each constituent to that calculated from the formula of the compound may be taken as a measure of the trustworthiness of the method employed, assuming reasonable skill and care on the part of the analyst. No such corroboration is to be had for such indeterminate mixtures as most technical products and articles of commerce, and beyond a presumption from a knowledge of their usual composition, one can be guided only by the agreement of duplicate analyses. Should the analysis be a complete one, the correctness will also be indicated by the equality of the sum of the weights of the constituents with the weight of the substance taken for analysis; in other words, when the sum of the percentages is exactly one hundred. This rarely happens, and then only by chance, except of course when one constituent is determined by difference. Presumably the nearer the sum approaches the theoretical total, the more accurate are the several determinations; but neither is this evidence conclusive, since a large positive error on one may have offset an equal negative error on another, and so the total be not seriously affected. Similarly, determinations made in duplicate may closely agree though each have been vitiated by a defect in the method, impurities in a reagent, etc.

As a rule a direct method is the most unequivocal, though quite as correct results may be obtained by the indirect methods and with more expedition and less labor; the field of the latter however is comparatively quite limited. The accuracy of an estimation by difference depends of course on the correctness of the determination of *all* the other constituents, and is unallowable for one forming only a small yet important component of a material, as a cumulation of errors on the others would seriously affect or even extinguish it. On the other hand, where an element or compound forms almost the whole of a material, the percentage as found by difference may be more exact than can be expected from the most careful direct determination — instance the metallic lead in the refined lead of commerce where the sum total of the impurities may not exceed .03 of one per cent.

On examining records of analyses of substances of every variety, made by chemists of undoubted skill and long experience in their special departments,

and with every facility at their command, we find that on the whole under these most favorable conditions a result of from 99.80 to 100.20 per cent of the element or compound determined is considered excellent; from 99.50 to 100.50, quite satisfactory; and a variation of one per cent or much more is not uncommon. Of course when the body determined forms only a part of the substance analyzed (as is always the case in practical analyses) the error is apparently reduced in proportion, and for comparison with the theoretical content all the percentages should be recalculated to a basis of 100. It is plain, however, that no comprehensive conclusions can be drawn from results on special material, and the figures given above can only be taken as a guide in a general way.

Of late years there have been many attempts made to define the limits of allowable inaccuracy for special determinations. A few of these are quite moderate in their demands, but more often the bounds have been made so narrow as ordinarily to be attained only by the specialist working under the most favorable circumstances — seldom by the general analyst less familiar with the methods and perhaps handicapped by want of appropriate appliances and frequent distraction of his attention. Reasonable limits would appear to be the extremes of a large number of determinations made by different chemists of moderate skill and experience following one or more methods as the case may be, expunging any results distrusted by their authors or clearly abnormal. But it will often be found that the limits laid down by even the most liberal of these are more closely drawn than the variations of a symposium of this kind would justify, and we must conclude that they are based chiefly on the most concordant of a number of duplications from the hands of those well acquainted with the methods for the particular substance in hand; while not a few are apparently only the expression of a personal opinion, unsupported by adequate experimental data.

On the whole, while they may be interesting to the beginner as evidencing the possibilities of a refined analysis, beyond this their value is seriously lessened by the objections mentioned above.

Examples of some comparative analyses made by a number of chemists using different methods or modifications for one sample may be of interest; several of these have not been heretofore published for certain reasons. However the important proviso, namely, that the parts of the original material sent out for analysis were assuredly of identical composition is in many cases open to doubt; indeed, where fine subdivision of a heterogeneous solid is not practicable, there will always remain a suspicion that the portion received by one chemist may differ from that of another so far as to cause a considerable difference in their results.

1. Thackray distributed two sets of drillings of medium hard Bessemer steels. On the first sample 23 chemists reported 36 determinations of phosphorus ranging from .045 to .055 per cent; 60 per cent of the determinations were between .049 and .052, and the general average was .0498. On the second steel 23 chemists reported 36 determinations from .076 to .091; 75 per cent of the results ranged from .080 to .086, and the general average was .0838. Drillings of a steel plate were sent by Jones to 9 chemists who made 19 determinations of phosphorus; the highest was .067, the lowest .060, and the average .064. There were 14 results between .062 and .065.

2. On a Bessemer pig iron from Bachman, phosphorus determinations were made by 16 chemists who returned 42 determinations from .096 to .165. He remarks: "To sum up, I find of three chemists working the acetic and citric acid method, two are wrong. Of three who worked the direct molybdate

method, two are wrong. Of two working the modification of the molybdate-magnesia method in which there is a large quantity of chlorides present with the nitric solution when phosphorus is precipitated, both are wrong; and of ten working the method so that there is only nitric acid and ammonium nitrate present with the ferric solution, nine are within the limits of error" [apparently ± .005 per cent].*

3. On two bottles of drillings "from the same plate of open-hearth steel" sent out by Kent, 11 chemists returned 23 determinations of manganese ranging from .30 to 1.14 per cent (!).

4. Samples of a low grade spiegel-eisen prepared by Stone were analyzed by 18 chemists according to 12 methods and variations, and 60 returns tabulated omitting some that were doubtful. Arranged with reference to the methods employed, Williams' volumetric method averaged 12.85 per cent of manganese with extremes of 12.60 to 13.05; other volumetric methods, average 13.43, extremes 13.02 to 14.08; gravimetric methods where the manganese is weighed as pyrophosphate averaged 13.43 with extremes of 12.92 to 13.84; where the manganese was precipitated as the binoxide and weighed as trimanganic tetroxide averaged 13.79 with extremes of 13.03 to 14.47; all methods averaged 13.39 with extremes of 12.60 to 14.47. Hunt (*loc cit*) in discussing the results observes that it was "very unfortunate that the material was not crushed and put through a one-hundred-mesh instead of only a forty-mesh sieve" before distribution, and believes that imperfect sampling will account for some of the discrepancies.

5. An artificial mixture of copper with various other metals, arsenic, sulfur, silica, etc., representing a material more complex and difficult of analysis than ordinarily would reach the chemist, was prepared by Eustis. Seventeen chemists reported 45 determinations of copper by seven methods, the lowest 43.90 per cent, the highest 53.34 per cent; 29 of these were between 46.50 and 47.50. On borings of pig copper sent out at the same time seven chemists returned 17 tests showing 91.07 to 98.17 per cent of copper, and five chemists 11 determinations from 94.38 to 94.92 per cent.

6. A large number of assayers examined samples of copper matte and borings of ingot copper received from Raymond.† A summary of their results follows, the figures for gold and silver in ounces per ton of matte and the copper in percentages.

	Determns.	Highest.	Next.	Lowest.	Next.	Average.
Matte — silver	26	135.38	131.22	122.88	123.03	127.87
" — gold	26	2.41	2.40	1.85	2.05	2.24
" — copper	16	55.17	55.08	50.55	50.75	54.11
Borings — silver	27	164.14	164.05	147.40	148.50	157.29
" — gold	26	.50	.42	.205	.21	.307
" — copper	8	98.46	98.19	97.04	97.37	97.69

7. A ground oak-bark was divided among six chemists all of whom were more or less experienced in tan analysis. By various modifications of the hide-powder process, 16 determinations showed from 9.73 next 9.90, to 11.42, next 11.40 per cent of tannin. By Loewenthals process and modifications, 7 results showed from 6.40 next 6.49, to 9.60 next 9.50 (Neubauer's factor ?). By various other methods, 5 determinations showed 5.11 next 5.70, to 17.20 next 16.02. The average of the hide-powder, Loewenthals, and other methods were respectively 10.01, 8.99, and 11.39.

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* Chem. News, 1889—2—115 and 131.

† Trans. Amer. Inst. Min. Engrs. 1896—252.

8. Four chemists and two laboratory assistants assayed a liquid proprietary medicine for morphine sulfate. Of the twelve results the highest (in grains per fluid drachm) was .102 next .098, the lowest .067 next .074, and the average of all .085. The samples sent out were parts of a mixture of several bottles of the medicine.

9. A sample of baking powder of doubtful quality was distributed among 7 chemists for analysis including a determination of starch. Of 10 results the highest percentage of starch was 30.50, next 29.91; the lowest 26.10, next 27.72; and the average 28.84.

10. Not to unduly extend these examples, I will present but one more, that of a mixture of oils prepared with great care to insure homogeneity. Three lots of the original mixture were sent out. Of the first lot, 15 determinations by 6 chemists showed from 98.72 to 103.42 per cent of one (unsaponifiable) oil (calculated to the basis of 100 per cent), 80 per cent of the 15 being within 99 to 101.5 per cent. The second lot to 5 chemists resulted in 11 determinations ranging from 61 to 177 per cent, and only 45 per cent of the 11 being within 96.5 to 103.5 per cent. Of the third lot, sent to 8 chemists, 14 determinations were returned ranging from 93 to 108 per cent, of which 57 per cent were between 98 and 103 per cent.

It will be seen that the results on the first lot agreed remarkably well considering the nature of the mixture, the third was only fair, while the second could hardly have been worse. Let those reconcile such contradictions who can — to me they but illustrate the futility of attempting to draw conclusions from data so influenced by the personal equation. It seems folly to allow the result of a tyro, perhaps his first essay, to weigh equally against one of a master long practiced in the particular field of analysis relative to the sample examined, or a perfunctory grind against a careful conscientious effort at the best possible issue — yet who would welcome the task of deciding how much weight should attach to the respective results on the basis of compentency and attention?

Standard methods. There are many determinations, especially in proximate organic analysis, where the methods are so complicated or defective in one way or another, or for other reasons, that it is often difficult for different chemists to obtain reasonably concordant results when working on one sample, and disagreements, annoying and often expensive, may arise between a buyer and seller, each party insisting on the recognition of the analyses most favorable to his interest; and although such differences are readily understood by those acquainted with the limitations of the art, they are certainly not conducive to a high respect for the utility of applied chemical analysis in general on the part of those engaged in business or in other professions.

To provide a means for preventing and settling disputes of this kind as far as possible, a number of chemists engaged in any one line of technical analysis may agree to accept as an arbiter a designated method whose details are specifically set forth, the results by this method, when all the minutiae have been scrupulously observed, to take precedence over those by any other. Should the method gain general acceptance among trade chemists or be indorsed by a society of specialists, it is known as an "official method."

However, it must be observed that the advocates of this measure are not as yet agreed as to just what character of a method shall be made standard or official, some insisting that every other consideration shall be subordinated to

that of accuracy; others propose that to be more practically useful the highest degree of accuracy may be waived if necessary, if thereby in point of time and attention demanded, the method may become a practical laboratory process and adoptive to the exclusion of all other methods for both routine and occasional analyses. Others again would go so far as to simplify it, even at the expense of other considerations, to the extent that the least expert should have no difficulty in following the directions. More conservative commentators point out that as the object is primarily the unification of results, it is a matter of indifference whether such harmony is secured by means of similar or identical methods or otherwise.

In favor of the establishment of standard methods it is urged that expense, friction, delay and ill-feeling are avoided by providing a ready and certain means of adjusting differences in a commercial transaction or wherever values are to be ascertained or confirmed; that the thorough investigation to which the provisionally established methods will be subjected cannot fail to determine what details are essential and what can be omitted or changed to advantage; and by relieving the chemist of the doubt and anxiety engendered when the correctness of his work is questioned by himself or others, he is spared the labor of many confirmatory analyses.

But there are not a few chemists, and of high standing, who regard the matter with disfavor, believing that disputes of this kind can be readily settled by a consultation of the chemists concerned or by a third party as an umpire. Their objections may be summarized —

1. That the spirit is antagonistic to the individuality that should dominate the conduct of an intellectual art, evidenced by the determined opposition that has met every attempt to codify the practice of other arts.

2. That the object is avowedly the unification of results, while a more rational endeavor would be the discovery and perfecting of scientifically accurate methods — the former does not always imply the latter.

3. That an official method will not only be resorted to for the adjustment of disputes, but for various reasons will be adopted by a large proportion of chemists for both routine and occasional analyses to the exclusion of other methods. It will be the exception that a method of this type can be so framed as to recognize other than the normal and usual constituents of the class of substances analyzed, so that an unusual constituent or impurity of great practical importance might readily pass unsuspected that would no doubt have been discovered had several different methods been focused upon it as would follow when each chemist employs such a method or modifications as he believes most competent — an instance is cited by Allen.*

4. That discrepancies have ever been an incentive to investigation as to their cause and remedy, resulting oftentimes in an original or more satisfactory method. With a standard method in vogue this stimulus is lacking, and it is feared that more will rest satisfied with the probability of an agreement with other chemists than will undertake the task of confirming their results.

5. Possibly what appeals with most force to some who dissent is the recognition that so far as the practice of any art, handicraft or business is reduced to fixed rules, in so far is it always relegated to those whose only qualifications are the ability and willingness to mechanically follow directions; and in so far as the practice passes into the hands of the uneducated and descends to the plane of a mere subservience to recipes will scientific research in the field

* Journ. Socy. Chem. Ind. 1884—2, 17.

of chemical analysis decline. Moreover, this class, satisfied with a smaller return for their services, will be given the preference in industrial laboratories over those who justly feel that the time and outlay for a liberal technical education should be recognized.

Whatever opinion one may hold as to the wisdom of establishing official methods, it is certain that the need has been exaggerated, more especially in the field of metallurgical analysis. From much of what has been written on the subject one unfamiliar with technical and industrial analysis would be led to suppose that in transactions based on analyses of commercial materials, discordances between the chemists of the producer, dealer and purchaser are the rule rather than the exception. As a matter of fact their proportion is but small, and in nearly every case can be traced to one of three causes: imperfect sampling done by ignorant or careless samplers, analyses hurried or neglected through press of other work or made by incompetent or perfunctory operators, and the effort of one of the parties to the transaction to obtain an unjust advantage of the other. With these faults a standard method of analysis should have nothing to do — the remedy should come from other directions.

Taking all things into consideration, a conservative view would seem to sanction the temporary establishment of standard methods for all determinations where a reasonably accurate method is lacking, or where the personal error comes greatly in evidence, thereby assuring results at least concordant. But where we have one or more reasonably accurate methods for a determination, it would appear more profitable to devote the time and labor of establishing a standard method to the many analytical problems for whose solution there is a pressing need.

Standard materials. Some who would hesitate to indorse the establishment of official methods have proposed the preparation and distribution of standard lots of staple articles of merchandise or technical products of average character and quality. Provided in large quantities with ample precautions against heterogeneity, a portion of each may be at the disposal of every chemist desiring it. If the results of analyses by a large number of chemists agree with reasonable closeness, the average is assumed to represent the true composition, and the material is then available as a referendum by which to determine the quality of a new method and its rank among those in common use, or in important analyses, as a substitute for a synthetic proof.

Viewed in its entirety, one cannot fail to perceive how asymmetric has been the growth of quantitative analysis. Along certain lines the progress has indeed been rapid, and the present status, if not all that could be desired, may at least be deemed satisfactory. In other departments the methods are fewer and their scope more restricted, to be employed with caution, and the results of analysis put forth under the proviso that great accuracy is not to be expected.

Again, there are many bodies for which methods of analysis will be sought for in vain, or at best but a few dubious makeshifts unearthed by patient search of chemical literature. Were these bodies of minor importance from both a scientific and practical point of view, their neglect would be easily understood and of less consequence. But unfortunately, a large proportion are of great interest and value to metallurgy, medicine, animal and vegetable physiology, agriculture and other sciences and arts, and to

special departments of technology, and reliable plans for their separation and determination would be welcomed as the key to many of the problems that now appear otherwise unsolvable.*

That the art has not attained the breadth and congruity that could reasonably be expected as compared with other arts of equal age may be due in part to the following:

Excluding physical methods, in proportion as a body is chemically active and pronounced and positive in its relations toward reagents, the more numerous, varied, and satisfactory will be the methods that can be and will be designed for its determination. Per contra, bodies that are nearly related in chemical properties offer peculiar difficulties toward separation, enhanced when they are of an indifferent or negative character.

That the determination of a body will further some practical end or prove an advantage in a financial way is always a stimulus to the invention and perfection of methods therefor. So potent is this influence that the great majority of methods are designed for a direct application in the arts or commerce. This would be of no particular moment were it not that such methods are for the most part special in their nature, unsuited, without more or less modification, to general analysis; and however useful to the specialist, cannot prove as beneficial to the art as would those more comprehensive.

The subordinate position to which analysis is often relegated in the curriculum of those pursuing a scientific course of study. How often is the "fetish of organic research" or theoretical or physical chemistry allowed a disproportionately large share of the time of the student availiable for chemical study and practice. It is difficult to assign a reason for this preference; the unbiased cannot but admit that quantitative analysis — in essence the derivative of other branches of chemistry and of physics — affords the student a broader and more comprehensive training than that of any other department. The principles of the atomic hypothesis and the laws of stoichiometry, accepted hitherto by the student as abstract propositions, are illustrated and verified; an acquaintance with the principles of general chemistry and many of its practical applications, the synthesis and purification of organic and inorganic compounds, the deportment of elements and compounds singly and conjointly, are all to be acquired by whoever essays to be a successful analyst; in the practice of the art is acquired a manual training in the use of instruments of precision, the perceptive faculties are sharpened, and the discipline of close attention to details and habits of careful observation enforced by the

* For example: "At the present time the whole subject of pepsin-assay is in a very unsatisfactory, not to say discreditable condition." "*. . . . that chemical analysis has failed to discover any process whereby the physiological action of these [drugs and toxins] on the human economy can be predicted has led to the hardly more satisfactory physiological assay". "The skillful adulteration of wine is extremely difficult to detect by chemical analysis". "Perhaps no determination is more unsatisfactory than the one [nitric acid] in question". "The complete analysis of a colouring matter is, generally speaking, one of the most difficult subjects which can be placed before a chemist". "No problem of greater difficulty will confront the chemist than the separation of such complex bodies [plant constituents]". "Results [on certain animal bases] varying among themselves over 100 per cent. . . . . do not cause us to have a very high respect for analyses of this kind." "As a consequence, the great majority of the published determinations of caffeine [in tea, etc.] are completely worthless. . . . " Such unanimity as to the want of reliable methods for many well known articles is rather depressing. The prevailing pessimism is relieved by the claim of Benedikt (Die Analyse der Fette und Wachsarten, Lewkowitsch's translation) that the analysis of fats "presents an almost complete system" though unfortunately he appears to have no supporters for his assertion, at least if the word system be interpreted to imply comprehensive and reasonably exact schemes for the analysis of complex mixtures.

failure inevitably following their neglect. Finally, the satisfaction of noting the development of one's skill in manipulation, and the pleasure derived in confirming deductions from a theory or duplicating the work of abler hands combine to make the study attractive as well as instructive.

The paucity of reliable methods may be charged in part to the misdirection of the efforts of the practical chemist. How often are time and labor spent in the elaboration of the minutiae of a special method that would better have been directed toward solving some of the problems that so frequently perplex the analyst. Particularly is the technical and industrial chemist remiss through his neglect of investigations toward the discovery of methods of proximate analysis for inorganic substances, content with pursuing the conventional routine of elementary analysis.

And the benefit derived from the invention of methods of proximate inorganic analysis would not be confined to the enrichment of analytical resources only, for to the practice of metallurgy and kindred industries the means of determining the proximate composition of their products would be of the highest service.

As an illustration, witness the voluminous literature recording perennial attempts to perfect methods for the determination of phosphorus in iron and steel that shall be at once rapid, accurate, and reliable. Granted that such a scheme would somewhat reduce the expenses of a technical laboratory or perhaps be desirable in other ways, it is certainly a matter of far less practical advantage than the invention of methods of proximate analysis of iron and steel, however crude; for on metallurgical grounds it appears highly probable that the proximate composition is more potent in establishing the physical qualities of the metals than the absolute proportions of any or all of the elementary impurities. Had but a part of the efforts in this direction been turned to a systematic endeavor to demonstrate the composition of these complex alloys, we might be confronted with fewer mysterious failures in service, fewer triumphant survivals of long and hard usage by material that would unhesitatingly have been rejected as unsafe or unsuitable if prejudged by an ultimate analysis.*

For the future, the trend of progress of the art will undoubtedly be in the direction of proximate analysis. Ultimate analysis, both organic and inorganic, has reached a stage where it may be left to the steady continuous growth that will naturally come. But the call for proximate methods is urgent for there are problems innumerable in all departments of the sciences and industries that can only be attacked through a knowledge of the exact proximate

* "That other [than mechanical and heat treatment] and now unguessed conditions profoundly alter both the mineral species and the structure of steel, as of crystalline rock, in most complex ways, is indicated by the utterly anomalous relations between the ultimate composition and the mechanical properties of steel. This anomalousness which has puzzled so many is readily explained by the close resemblance between the conditions of the formation of rock and ingot which not only show us why we do not discover these relations, but that in all probability *we never can* from ultimate composition. The lithologist who attempted to-day to deduce the mechanical properties of a granite from its ultimate composition would be laughed at. Are our metallurgical chemists in a much more reasonable position? . . . . . In vain do we flounder in the sloughs and quagmires at the foot of the rugged mountain of knowledge seeking a royal road to its summit. If we are to climb, it must be by the precipitous paths of proximate analysis, and the sooner we are armed and shod for the ascent, the sooner we devise weapons for the arduous task, the better."—Howe.

composition of the complex materials involved, ultimate analysis failing to afford the least aid in their solution. Not that a proximate analysis can alone and at once clear up the many vague ideas as to the relations of these complex bodies or interpret their frequent anomalous and capricious behavior under certain conditions, but through the information afforded the microscopist, physiologist and technologist, the solution will be made possible.

What means the future investigator will employ to accomplish this end can only be conjectured. A number of analytical processes for one reason or another have not received the attention they deserve and have been applied to only a few of the many purposes for which it would appear that they could be turned; among these are the separation of inorganic bodies by immiscible solvents, now so successful for organic compounds; the electrolysis of organic bodies, yielding liquid or gaseous decomposition products; separation by electro-dissolution; the selective action of certain reagents in solution or precipitation; transformation by micro-organisms or ferments; the measurement of progressive inherent or incidental changes in organic bodies; and new applications of cryoscopy, capillarity, osmose, dissociation by heat in vacuo, etc. Possibly purely mechanical processes may be so refined as to be capable of giving reasonably sharp separations. To the study and practical application of such means as these may the attention of the student be directed with a better prospect of success than in attempts to apply the more familiar principles.

But it would appear that our present resources however they may be extended are entirely inadequate to the task, and any great progress in this direction must come through the discovery and application of new principles of analysis.

APPENDIX.

TECHNICAL AND INDUSTRIAL ANALYSIS.

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Few if any of the liberal arts have contributed so largely to the advancement of the sciences and arts in general as has analytical chemistry and its branches. In sanitary science and hygiene the public welfare is conserved by the detection of adulterated foods and unwholesome waters; the physician and pharmacist are provided with materia medica of trustworthy strength and purity; the agriculturalist learns, though somewhat imperfectly as yet, what elements of the soil are most essential to specific vegetable growth and if absent or exhausted, and the nature and comparative value of fertilizing additions; the engineer as to the formulae to be specified for the composition of metals reliable under strain and shock, the calorific value of fuels, the quality of lubricants and anti-friction bearings, and the nature of boiler waters and their correctives; the miner and smelter, as to the grade of ores, their valuable associates and detrimental impurities, and the processes most suitable for their reduction. Besides these it proves oftentimes an almost unimpeachable referee in legal complications deciding contentions that are otherwise unsolvable.

Again, in technology and manufacturing it can safely be said that every department of industry, outside those purely mechanical, has profited by its aid. It is not difficult to perceive how a knowledge of the exact composition of such articles as enter into the processes of manufacturing will afford a rational basis for their treatment and disposition, and to this end has the attention of manufacturers been directed during recent years. Less familiar, however, are many other applications which from their specific nature or for other reasons are slow to become known to the public.

The material with which the practical analyst has to deal may be roughly divided into two classes. The first includes naturally occurring and factored articles of which he is to determine the composition and advise as to the value and adaptability to a given purpose, or to certify as to the presence or absence of deleterious associates or adulterants. Analyses of this nature ordinarily fall in the province of the commercial or sanitary chemist. To the second class belong the raw materials and intermediate, final, and waste products of manufacturing processes, for whose analysis provision is made in the way of special laboratories adjunct to the manufactories.

As in other arts, the occupation of the commercial chemist is usually confined for the most part to some one analytical specialty, on which he endeavors to build a reputation and become known as an authority, selecting either the assaying of gold and silver ores and their products, the examination of natural waters, iron and steel, sugar, brewing materials, tanwares dyes, etc. In proportion as his reputation for ability and probity enhances, his counsel is sought on technical questions, the advisability of investment in the numerous projects continually being proposed to the capitalist, and as an expert

in the valuation of mining and manufacturing properties and other lines of business enterprises.

But it is not the rule that he can command so large a clientele in his chosen department as to be able to devote his time to it exclusively, and he must be prepared to undertake commissions in any line of technical investigation and counsel — usually more remunerative than analysis alone.

The occupation of the sanitary chemist or public analyst is mainly the examination of foods and condiments for adulterants and substitutions. Many large cities and some States have established laboratories under municipal or State control and employ one or a corps of chemists who periodically report on the condition of the water supply of the city and the purity of the ice and foods sold in the open market. Of the latter, milk, so easy to dilute, naturally claims the most attention, although the substitution of butterine for butter, and chicory or artificial berries for coffee, and the vending of exhausted spices, inferior drugs and proprietary medicines of a dangerous character are not uncommon. The wholesomeness of potable waters is often to be passed upon with recommendations as to the feasibility of purification if below standard, or whether one of normal purity is in danger of contamination by reason of the proximity of drains or sewers. In addition to the ordinary duties of his office he may be asked to examine the ventilation of public buildings, to superintend the disinfection of places offensive or dangerous to health, or to decide whether the manufacture, storage or transportation of articles that are inflammable, explosive or offensive should be permitted within certain districts, etc. Supervision by competent chemists supported by police authority has resulted in abating the spread of certain contagious and infectious diseases to a gratifying degree.

The bureaus of agriculture in many countries and most of the United States have instituted laboratories for investigation and experiment on the composition and aggregation of soils, the relative food value and yield of different varieties of plants and the processes of manufacture best suited for their preparation for the market or the extraction of their essential principles, the comparative value of fertilizers, insecticides, etc., and kindred problems. Analysis is confined mainly to a few departments except where needed in the course of investigations. The chemists of the agricultural stations in the various States, in conjunction with those of the United States government, have for some years maintained an association, one of whose objects is the formulation of official methods of analysis for the materials and products of agriculture. Several other countries have similar organizations.

Chemical engineering. There are many lines of manufacturing wherein the processes are based essentially on chemical transformations of raw material to finished product, and in these establishments the chemical engineer is an important official. Again, there are many classes of factored products whose commercial value varies in proportion to their purity or is based on certain characteristics of color, odor, flavor, clarity, etc., such as crude and fine chemicals, paints, oils, soaps, beverages, spices, relishes, medicinal and proprietary articles, toilet requisites and the like, and to these his services are not less valuable.

In works of this kind all the processes were formerly conducted by the light of experience, and within their limitations, and so long as the established practice remained unchanged, a fair and not infrequently a remarkably good and uniform quality of the various products was ordinarily attained. But to disturb this routine there would occur from time to time an inability to secure raw materials from the source formerly constituting the entire supply, the in-

stallation of more modern machinery or appliances, a change in the personnel of the management, a demand by the purchasers for some change in the composition or characteristics of the products, or the necessity for a reduction in the cost of manufacturing due to competition or an advance in wages or the prices of raw material. At such times many difficulties were encountered in modifying the general conduct or details of the processes to meet the new conditions and frequently the quality of the product suffered in the interim.

Under the modern system of chemical control, changes of this nature can be anticipated and provided for, and come into effect without interfering with either the quality or output of the product. And although in some industries exact information as to the reactions on which the conversions are based is yet wanting, enough is known to outline the changes and to learn the effects on the product of modifications in the practice.

Direction of both the chemical processes and the mechanical appliances is intrusted to the chemical engineer, and in some establishments he has also a general supervision of the labor. He must be well acquainted with the details of manufacturing and machinery to be competent to modify and improve them as circumstances warrant, to plan and provide for the manufacture of new products, and in case of accident to contrive temporary expedients that the operation of the plant may proceed without interruption.

In the smaller manufactories such a position can be filled to advantage by one person, but for an establishment more extensive and where the products are numerous and varied, many believe it a better policy for the chemist to delegate the care of the power and machinery to an assistant, a competent mechanical engineer. For in these days of rapid development and sharp competition better service can undoubtedly be rendered by those whose training and experience have been confined to one specialty. Few there are who can master two professions, and mediocrity in both is hardly a qualification for the exacting demands of the modern factory.

In many establishments not engaged in manufacturing beyond repairs for the maintenance of their plants, large quantities of incidental supplies of various kinds are purchased as needed. Formerly they were bought under the stipulation that the quality should equal that of some well known make recognized as of a uniformly high degree of excellence. On receipt of a purchase, it was inspected by some employee experienced in the use of the particular article, and his decision as to whether it conformed to the grade contracted for was conclusive as to acceptance or rejection. Sometimes a rough and often perfunctory practical test was made on a small scale, where inspection alone left a doubt.

But it was generally admitted that such a superficial examination was inadequate, often failing of vindication when the article was put into practical use and incompetent for the detection of the many ways of depreciating the quality without affecting the general appearance; so that in later years the purchaser has come to rely more and more on chemical analyses and physical tests, which, made by competent inspectors, will often at once and finally settle all questions as to quality, purity, and commercial value. And generally, the consumer, through his ability to discriminate between the wares of different dealers, receives a higher grade and more uniform quality than formerly, for the fact that a purchaser has instituted a laboratory soon becomes known to the seller with the immediate result of an improvement in the quality of supplies furnished. And constrained by the demands of buyers or the example of competitors to be able to certify to the exact quality of what he has to sell, the producer or

broker must resort to the commercial chemist or install a laboratory of his own.

Within recent years the manufacturers of certain products have become convinced that chemical analysis could be made a valuable aid in the conduct of their business, and through having at first an occasional analysis made by a commercial chemist, have found it good policy to equip and maintain works-laboratories wherein one or more chemists are engaged in analysis and the investigation of matters appertaining to the processes in use.

In every manufacturing or refining process, exclusive of those that are strictly mechanical, the progressive changes undergone by the raw material in transformation to the finished product may be followed to decide what particular system of conversion will be most efficient and economical, and discover where modifications can be introduced with advantage, and to what extent waste products may be impoverished or turned to account. And a lapse in the fidelity of the workmen or an impaired condition of the machinery or other appliances or an increase in the cost of production at some stage of the process may frequently be exposed or traced by a few simple chemical tests. In some establishments every step in the processes of manufacture is watched from the laboratory, the guides of tradition and personal opinion, often groundless or chimerical, being everywhere supplanted by the rational and exact basis of analytical chemistry.

It is probable that the plan of analytical control originated in the laboratories of manufacturing chemists, though carried out to a limited extent only, hampered by a lack of adequate methods of analysis. Next followed the smelters of iron, the adoption here more successful since the processes of reduction deal only with inorganic bodies and the chemical reactions of smelting are comparatively well known. The iron and steel industries still lead all others in the number of chemists employed and the thoroughness with which the technic is controlled. Of other manufacturers that have later followed their example to a greater or less extent may be mentioned the producers of paints and varnishes, sugar and glucose, explosives, soap and candles, glue, rubber goods, glass and pottery, wood-pulp and paper, dyes, dyed fabrics, baking powder, spices, smelters of base and precious metals, refiners of oils, meat packers, etc.

For an illustration, the routine chemical work of the laboratory of an iron and steel works may be described in some detail. A large steel works producing rails or plates may regularly employ as many as a score of chemists occupied about as follows:

1. In each cargo or shipment of iron ore received is determined the percentage of moisture, metallic iron, phosphorus, and sulfur, these being the most important constituents. Silica, the earths, and other constituents are also determined on each cargo unless the ore comes entirely from one large mine, when less frequent tests will suffice. The receipts of fuel — coke, charcoal, or anthracite — are regularly tested for sulfur and ash, and the limestone for lime, magnesia, silica, and sulfur, and for other impurities when called for. In the spiegel-eisen or ferro-manganese (the carburetter) the manganese, phosphorus and silicon are the constituents usually determined, the carbon and iron being present in a fairly constant proportion in any given grade (*i. e.*, percentage of manganese) of the metal. The miscellaneous scrap iron or scrap steel for charging the open-hearth furnace is sometimes analyzed, but usually is in a form that does not admit of fair sampling.

2. The pig-iron made by the blast furnaces is regularly analyzed for silicon, sulfur, phosphorus, and manganese, and for carbon and other elements as may

be desired. In works where the iron is not cast into pigs but is carried in a molten condition from the blast furnace to the converter or open-hearth furnace, the silicon and sulfur are to be determined as quickly as possible after the metal leaves the blast furnace. Of the furnace slags a complete analysis is made on the average of all the tappings during one week, or oftener if thought advisable. The furnace gases are regularly or occasionally examined for the ratio between the carbon monoxide and carbon dioxide.

3. From every heat of steel from the converter or hearth is dipped a small ingot which is tested for carbon, silicon, sulfur, and manganese, except where rail-steel is the product, when the average of the heats from each turn of twelve hours is usually thought sufficient for the three elements last named, the uniformity of the steel made depending largely on the correctness with which the ores, fluxes, and metals have been examined and weighed into the furnaces. The converter and open-hearth slags are weighed and analyzed occasionally as a check on the inevitable loss by permanent oxidation of the metal of the bath and from metal globules retained mechanically. In open-hearth furnace practice, rough tests of the metal of the bath are made periodically at intervals of an hour or less to determine the rate at which the carbon is being oxidized to carbon monoxide and leaving the metal; and where the hearth is neutral or basic, similar tests are made for phosphorus as it oxidizes and passes into the slag.

Should the proportions of the valuable constituents in a raw material be found to fall below, or of those deleterious to exceed the limits agreed upon at the time of purchase, a concession in price is demanded or the entire lot is rejected. The charges of ore, limestone and fuel fed to the furnaces are calculated from their analyses to produce the composition of pig iron desired, and to furnish a slag that shall be fusible at a moderate furnace temperature and remove as much as possible of the sulfur of the charge, thus insuring an output limited only by the capacity of the furnace, and produced at the lowest cost. From the analyses, any hitch or abnormal working of the furnaces, cupolas or vessels is shortly detected; and the product can be placed on the market with confidence that the impurities are within the stated limits, and, as far as composition is concerned, will uphold the reputation of the makers. And since a complete chemical record is kept of the product, in the event of a failure in service resulting from undue hardness, rapid wear, heterogeneity, or similar fault, the precise cause of failure may be more readily located.

4. In addition to the above are examined the refractory materials used in lining the furnaces and ladles; the coal for gas-producers or liquid fuel for boilers; spittings or splashes of iron and steel from the converter; furnace-fume; washes for coating moulds; and various other materials and by-products. Doubtful or apparently incongruous analytical results obtained during the rapid routine work of the laboratory are to be repeated by more accurate methods. Special analyses are to be made of iron and steel that is designed for exceptionally severe strain or wear or of that which has failed in service, and the products of competitors, as well as examinations of articles of the most varied nature at the request of those in authority.

All this calls for a great amount of analytical work that is turned out with a rapidity scarcely credible by one whose experience has been confined to analyses for scientific purposes only — in a large steel-works the number of determinations will often reach as high as 150,000 per annum. Yet the not inconsiderable cost entailed is amply repaid by the certainty and uniformity of the metallurgical practice as compared with the rule-of-thumb formerly in vogue.

The analyses made in a steel works may be divided into three classes: the

first comprises those where the highest accuracy is demanded and where ample time is allowed the analyst to secure it; in the second are those that should be at least fairly accurate, yet from their volume and the immediate need of the information they furnish must be completed in a limited time; and lastly, those that shall decide the further treatment or disposition of intermediate products liable or certain to rapidly deteriorate by chemical change or loss of heat—here immediate returns are highly desirable if not imperative. Even a rough approximation if quickly known may be of great assistance to the management. Recognizing that only constant practice will enable one to attain the greatest rapidity and surety, the analytical work is divided in such a way that each chemist is engaged at only one or a few kinds of determinations—thus three will divide the day of twenty-four hours, each making color-carbon tests of the steel produced during his turn of eight hours; three others the silicon and sulfur in furnace iron; one chemist analyzing all the ore received; another the slags, limestone and coke; and so on.

The great volume of analyses and the rapidity with which they are turned out has given rise to an impression that most, or at least many, of the results so obtained are at best but doubtful, even approximate accuracy being sacrificed to speed. Doubtless at works where a large output of the product is the highest ambition, with quality as a secondary consideration, the same policy extends to the laboratory; this, unfortunately common, is by no means universal, for it has come to be realized that a result to any extent doubtful is not only useless but misleading as well.

As to the comparative accuracy of the general run of works' analyses to those made under more favorable conditions it is difficult to speak positively. In their favor there is to be considered, first, that for indefinite periods the composition of each of the products and by-products of a well organized factory is so uniform or approaches so closely to that aimed at or calculated (except during brief periods of anomalous conditions) that the proportions of the various constituents are confined within certain fixed maximum and minimum limits, and knowing these, the works-chemist can simplify and shorten the more general methods or safely go so far as to employ those worthless for other than the specific material with which he has to deal; second, that forms of apparatus can be selected or specially designed that are convenient and adapted to the particular operations of an analysis, and being permanently arranged are in readiness at all times for immediate use; and lastly, that the chemist, engaged continuously in one line of work, becomes familiar with all the details and can carry on many analyses together without loss of time at any stage. Under these circumstances there would seem to be no inherent incompatibility between reasonable accuracy and exceptional speed.

The chemist is occupied mainly in the capacity of analyst in metallurgical and other works where inorganic substances are chiefly dealt with, since here the materials admit of rapid and exact analysis and the quality of the output under normal conditions of manufacture can be controlled and adapted to the market. But where organic bodies are the subject, as in tanning, dyeing, and the like, the actual chemical changes are but imperfectly understood and differences in the composition or physical character of the raw material and adjuncts or a variation in the routine of the processes, though perhaps so slight as to be unnoticeable, may greatly modify the habitus and general qualities of the product. Moreover, being often bodies highly susceptible to chemical change and prone to disorganize spontaneously or through external influences and so deteriorate or develop undesirable properties in the product,

a large amount of investigation and experiment is called for. To deal intelligently with such questions the chemist must be so conversant with every detail of the processes in use and the routine of the manufacture that in the laboratory he may be able to carry a sample of a raw material or intermediate product through a reproduction in miniature of the whole or a part of the process and to judge from the yield and character of the product (corroborated as far as may be by analysis) as to the completeness and success of the conversion, and to note any unusual behavior or characteristics that may have to be considered when operating on a larger scale; or to convince by actual demonstration that some modification or radical change in the process will be essential or advantageous for the material in hand.

It will not be necessary to detail the occupation of the chemist in the different industries of this kind; in all he is expected to examine and value the raw materials purchased and decide as to their suitability for the purposes intended, the nature of the impurities as regards their effect on the processes and products, liability to hasten deterioration on keeping, or influence in other ways; whether the material is usable in the form or state received or better after comminution, purification, drying, etc., and whether adapted for treatment by the usual processes or requiring some modifications; and to call attention to any peculiarities or unusual qualities he may observe. Further he is periodically to test the products in suitable ways that he may certify that the standard of quality is or is not maintained; appraise the waste products and advise concerning their disposition; experiment on any improvements that may occur to him or be brought to his notice; and in general, to give expert opinions on any subjects connected with the chemical side of the manufactory. Much is left to his discretion as to what extent it is necessary to carry an investigation to accomplish the end desired, and along what lines it is to be conducted.

Of the miscellaneous industries that in recent times have come to employ a large number of chemists may be mentioned the miners of iron ore. Here the principal occupation of the chemist is in analyzing the ore shipments for their content of iron and other important constituents. But in addition in many mines the output is divided into several grades classified according to the percentage of iron or some other constituent, usually phosphorus. The ore deposit is divided into sections bounded by rock-seams or timbering, and the surface of ore in each section periodically sampled and analyzed and the miners advised to what grade the ore belongs. Various other metalliferous ores are mined on a similar plan, and attempts have been made to chemically divide the yield of coal mines, asphalt beds, clay pits, etc.

The technical chemist has often to examine mixtures sold for sundry purposes in the arts that are wholly or partly organic and whose composition is kept secret by the makers. Such are proprietary articles designed for medicinal or toilet purposes, nostrums, factitious foods and condiments, food preservatives, water purifiers and boiler purges, fuels, metallurgical fluxes, tempering powders and physics, cleaning and polishing powders and pastes, etc., etc., that are continually brought upon the market vaunted as superior to all other preparations hitherto employed for the specific purposes. Some of these are of real merit, others plainly frauds by intention. As might be supposed, both classes are as a rule comparatively simple in composition, and to

those having some experience in the examination of mixtures of a similar kind, the analysis is attended with no great difficulties.

There is also a third class, unfortunately too common, of mixtures compounded, often in good faith, by those wanting in chemical knowledge and frequently in practical experience as well. Like the poly-pharmacist, they endeavor to incorporate every ingredient that has been proposed for the purpose with, perhaps, others that can lay no claim to efficiency and apparently chosen solely for their cheapness or the opportunity to purchase a supply at a bargain. It is not strange, therefore, that it is often beyond the ability of the chemist to solve the composition of such a hodge-podge, and any statement as to the relative proportions of the constituents but little better than a guess.

For the examination of material of this kind it is seldom that a search through chemical literature will reveal any scheme of analysis that can be adopted, or at best more than a few that may be doubtful or discredited, and the analyst must exercise his chemical knowledge and inventive ability to devise one that shall answer the purpose. It need not necessarily be so comprehensive as to include every constituent, since it is generally left to his discretion as to what extent the analysis should be carried to supply the information desired or to demonstrate the value or uselessness of the article for a particular end. If the essential ingredients and their approximate proportions can be discovered, the information will probably be sufficient for all practical purposes, and to this end should the attention of the analyst be directed—often the chemist is asked merely to supply a recipe for the preparation of an article equally as efficient for a given purpose as the sample furnished him; with perhaps the stipulation that between them there shall be a close resemblance in appearance, etc., for reasons not difficult to surmise.

However, any analytical method that can be devised will often prove inadequate for either a qualitative or quantitative analysis. For the former one must rely mainly on conclusions drawn from the general appearance and physical qualities of the sample, and nowhere is the faculty of acute perception of greater service than in the identification of certain constituents from peculiarities of odor, taste, consistency, hardness, mobility, appearance when magnified, etc., even though considerably modified by other ingredients introduced for legitimate ends or to conceal evidences of sophistication or inferior quality. Not less helpful are the hints afforded by a familiarity with the composition of other articles in common use for the same or similar purposes—in fact the chemist for the time being must assume the rolê of botanist, mineralogist, pharmacist, metallurgist or what not according to the problem before him.

For the quantitative analysis it is of course impossible to lay down any general plans of proceedure where the subjects are so varied in character, but it may be said that for the most part an actual separation of all the constituents is impracticable and that attributive methods have here a large application; often recourse must be had to mechanical separations, sometimes of the crudest nature. In the case of liquids, distillation and examination of the several fractions, especially the first, may give information as to volatile constituents. For powders or friable solids mechanical separation by sifting through various sized meshes, elutriation, vanning or jigging, will often serve to distinguish most or all of the constituents. Colorimetric methods can sometimes be employed for one or more members.

A scheme that has much to commend it is to first identify as many of the constituents as can be made out, then compound a mixture of these that shall resemble the original in physical properties, altering the proportions until a

close agreement is attained. If successful the approximate composition is already known and may be corroborated by an analysis of the sample; but if it is found impossible to prepare a fair duplicate in this way, the differences noted will often indicate where the qualitative deductions were incorrect or suggest the nature of the missing associates. And occasionally during the succeeding analysis as one constituent after another is disposed of, artificial mixtures should be compounded and compared with the original sample.

Prior to the actual analysis of a sample of this kind it is well to learn the particulars of the manufacture as far as they are made public or can be gathered from any source, the selling price, the directions for its use and any precautions in the application enjoined, for what particular features superiority is asserted and what defects in similar articles overcome. The general habitus of the sample furnished should be noted and any peculiarities of consistency, color, odor when cold or on heating, heterogeneity, alteration on exposure to light, air or moisture, the specific gravity, etc.

Observations such as the above, considered individually and mutually, will generally furnish clues to shape the course of the succeeding analysis. A practical test of the material, a study of the composition of similar articles, their selling price and the relative esteem in which the various makes are held by the public, and, if possible, a visit to the manufactory and observation of the processes of manufacture as far as may be permitted, may result in much pertinent information. In many cases it will be found more expedient to conduct the analysis on the material after it has been prepared to the state or condition as used by the consumer than in the original form as purchased on the market. Finally, a consultation with a chemist whose line of work is confined largely to materials similar to the one in hand may throw more light on an obscure point than days of research.

Investigations of this kind are most interesting, and although at times the outcome may not be all that could be hoped for, cannot but be highly instructive to the patient worker.

A class of articles frequently to be analyzed by the technical chemist is that of homogeneous mixtures of two or more analogous complex bodies incorporated in the liquid state. Usually the identity of each component is lost as regards any means of direct separation now known, though it is conceivable that in some cases perfect amalgamation is long deferred and that processes of differentiation might be discovered applicable at least to recent mixtures. But at present we are restricted to methods based on (1), the determination of a normally occurring constituent (either originally present or introduced in the technical treatment or developed by age) of one member, absent from the other; (2), the divergence in the proportions of one or more of the common constituents of the members; and (3), a measurable physical constant of unlike values in the members and persisting in the mixture. But it is to be noted that the proportion of any constituent may vary between wide limits and be a doubtful quantity, and that processes of preservation or purification may alter the proportion of any one constituent or entirely remove it from the mixture, or modify the value of a physical constant.

In the valuation of merchandise by analysis two cases may be presented. One is where the material examined contains but one constituent of value for the manufacturing or other purpose intended, and an assay of the material shows at once its money value as far as constitution is concerned. Usually the material is priced at a certain sum per 'unit', a unit being one per cent in most cases. Exceptions are where the constituent is in two or more forms or combinations that are of unequal value for the purpose

on account of the unlike treatment they must undergo in manufacturing, or where the cost of conversion, the losses sustained, or the quality of the product varies with the relative proportions. For example, a material from which the constituent is to be extracted by an acid, one part readily dissolves in a comparatively dilute acid, the other only in strong acid and incompletely even after long digestion at a high temperature.

The other case is that of material containing several constituents of more or less value for the purpose, or detrimental as the case may be; it is usually a difficult problem to determine to what extent each contributes to or modifies the value, and any schedule that aims to fix the relative values of the constituents and allow a calculation of the absolute or relative value of a given lot must be to some degree arbitrary.

The conduction of a sample of a raw material or intermediate product through the routine of the manufacturing process the material is to undergo must be done with much circumspection, and the results liberally interpreted, for it is doubtful whether the conditions attending factory practice can ever be exactly duplicated in the laboratory. It is well known that many processes yield products that differ more or less with respect to the amount of material operated on, certain secondary reactions that have a great influence on the product appearing only with a certain minimum of material; the unavoidable losses are nearly always less in proportion to the weight of substance treated; the application of heat, refrigeration, aeration, extraction by solvents and like operations proceed more uniformly and thoroughly on the large scale; these and other factors tend to lessen one's confidence in deductions from tests on the small scale. Many times have conclusions drawn from laboratory tests been flatly contradicted when the same operations were repeated in the factory. Generally speaking, the result of a miniature test is the more trustworthy in proportion to the amount of material treated.

As a prediction of the result of an analysis based on the general appearance and physical properties of the substance analyzed often proves fallacious, conversely due caution is advisable when attempting to infer mechanical or other characteristics from the chemical composition, for, contrary to what is anticipated, an analysis alone may afford no information whatever as to the general character or adaptability for a given purpose.

Qualities commonly regarded as distinctive and characteristic are not infrequently qualified or suppressed from various causes. Thus we think of steel as hard, an acid sour, silver white, and quartz vitreous; yet antecedent thermal treatment, degree of insolubility, atomic and molecular arrangement, the presence of associates known or unsuspected, etc., may modify or efface any of these attributes. In the large class of crypto-crystalline and fibro-crystalline bodies the influence of physical structure on their manifest properties is dominant — the shape, size, and juxtaposition of the crystals, their regular or segregated distribution through a matrix, their dowelling or interlacing where vicinal, the effects of progressive crystallization, fibration, granularity from enveloping shells, etc. Odor, flavor, aroma, are susceptible of modification by physical structure, as is well known, and color, the quality so often relied on to establish the identity or composition of a substance, often misleads. Illustrations are met with in commercial articles made up by different manufacturers according to one formula but markedly unlike in appearance.

In face of such disturbing factors it is a question how far a knowledge of the

composition will afford an insight to the properties of a substance or justify an opinion as to its practical value or utility. Plainly a proximate analysis will usually be a far more substantial basis for conclusions than an ultimate one.

Specifications. That the seller may be informed as to the grade of goods that will be accepted by the buyer there has been adopted by most large consumers the plan of submitting printed specifications that detail explicitly what tests and inspections each purchase must pass. According to the nature of the article the tests may be physical or chemical or both, with in many cases an additional stipulation as to general appearance or finish. Following are examples.

SPECIFICATIONS FOR GALVANIZED TELEGRAPH WIRE.

1. The weight of wire per mile to be approximately as follows: No. 4 gauge, 730 lbs.; No. 6, 540 lbs.; No. 8, 380 lbs.; No. 9, 320 lbs.; and No. 10, 260 lbs.

2. The tensile strength shall not be below 2.5 times the weight of the wire in pounds per mile.

3. The electrical resistance in ohms per mile at 68° Fahr. shall not exceed the fraction $\frac{4800}{W}$ where W is the weight in pounds per mile.

4. The wire to be circular in section, soft and pliable, and have a smooth surface. A piece 6 inches in length when gripped in vises and twisted must not break below 15 full twists.

5. The thickness and adhesion of the galvanizing will be tested as follows: the wire is immersed in a saturated neutral solution of copper sulfate for one minute, wiped with a cloth and examined; after four treatments in this way the wire must show no coating of copper. *

6. Not less than five samples will be taken at random from each lot of wire received, and tested by an inspector representing the consignees according to the above specifications. If more than 10 per cent of the samples fail to meet the requirements, the entire lot will be rejected and returned to the manufacturers.

SPECIFICATIONS FOR OLEINE: SPECIAL GRADE.

This grade of oleine will be bought on sample. Any barrels of a shipment that show a lower quality than the sample furnished will be returned to the shipper.

1. The oleine to be clear at 50° Fahr., the color light to medium brown, and the gravity at 60° Fahr. from .890 to .910.

2. The ash not to exceed .5 per cent.

3. The total free acid not to be below .95 per cent; hydrocarbon oils not over 3 per cent; and neutral fat not over 3 per cent.

4. The free mineral acids not to exceed .5 per cent, and the oleine not to contain more than traces of lead, copper, or arsenic, and not over .3 per cent of iron oxide.

5. Containers to be plainly marked "Oleine — Special grade". Samples sent with quotations not to be less than one pint.

Usually the chemist of the buyer draws up the specifications for the material purchased, availing himself of the advice of those directly concerned in its use and often of the sellers also. The specifications are revised from

* The zinc coating of the wire reacts with copper sulfate, the zinc dissolving and being replaced by an equivalent weight of copper in a loose spongy form that can be readily wiped off. Iron and steel also react with copper sulfate, but in this case the copper deposit firmly adheres to the wire and cannot be wiped off.

time to time as conditions of use and the market changes and practical tests and investigations advise, avoiding, however, frequent and radical changes as far as possible.

To formulate a specification that shall be equitable to manufacturer, middleman and buyer is not infrequently a matter of some difficulty. Many adopt the simple plan of averaging the results of the tests of all purchases during several previous years that have proved satisfactory in service; others select as a standard the products of some one manufacturer of acknowledged high reputation. And a few appear to rely entirely on their own opinions however opposed to the views of others fully as experienced and perspicacious as themselves. It is plain that to proceed intelligently in drawing up a specification one should be familiar not only with the practical use of the material but with the processes and limitations of manufacture as well. And all specifications should be interpreted not as hard and fast rules but as guides to be relaxed or modified as the case in hand appears to justify—yet it must be remembered that if the inspector is to be strictly impartial and favor no one of a number of competing sellers, he must fix and adhere to a uniform final limit with all, other things being equal.*

Undoubtedly there have been issued and are now in force specifications for certain materials whose quality would be better determined by the judgment of those familiar with the purposes for which they are intended. For in many cases those particular qualities that are most valuable to the user are as yet but imperfectly known from the lack of systematic and conclusive investigations. Again, a given material may be unusually susceptible to the treatment it undergoes during its application and while in service, the good qualities being conserved and the faults mitigated, or the reverse, according to the skill and care of whoever is directly employed in its application, use or preservation. So that widely differing opinions are held as to the composition or physical properties that are most desireable; and manufacturers of certain products have repeatedly claimed that the stipulations of a specification of this kind could be met by material of a lower grade than they would be willing to put on the market admitted as their own product. And there are some who, with this in view, would do away with specifications largely or entirely, asserting that as many of the qualities that earn for a material a deserved reputation cannot as yet be reduced to set phrases, the conscientious manufacturer has no recognition of his efforts to produce a superior article.

Yet although carried to an extreme by the injudicious, there can be no question that the plan of purchasing under specifications has on the whole been of great advantage to all parties concerned. Restricted to requirements that are reasonable and generally regarded as a fair criterion of quality and free from individual pet theories, there can be raised no valid objection on the part of the seller, and where close limits in regard to such matters as uniformity, durability, facility of application and the like can only be laid down somewhat arbitrarily, there should be asked no more than what is considered as moderate and reasonable by those best qualified by study and experience to form an opinion on the subject, thereby conserving the interests of the buyer and laying no undue hardship on the manufacturer.

Adulteration. A large share of the occupation of the technical chemist is in the examination of foods, condiments and beverages, drugs and proprietary

* The Manufacture and Properties of Structural Steel, 356.

medicines, and raw materials and products of the arts for evidences of an unadmitted debased quality.

As to what constitutes a prima facie case of adulteration with certain articles is to some extent a matter of opinion, and it is often left to the chemist to decide whether a certain constituent should be classed as an adulterant within the legal interpretation of the term. Practically, the laws relating to the adulteration, degradation and falsification of foods and drugs are based on the following premises.

1. The incorporation of any foreign substance to increase weight, bulk or strength, to conceal evidence of debased or inferior quality, or to confer a fictitious appearance, flavor or odor.

2. The omission or withdrawal of some valuable constituent, wholly or in part.

3. The presence, either originally, developed, or by addition, of a poisonous ingredient or one undoubtedly injurious to health.

4. The manufacture of any product from diseased or tainted flesh or decomposed fruit or vegetables.

5. So naming or describing an article of domestic production as to lead the purchaser to infer a foreign origin or that the article is of some well known superior grade or from a factory of established high reputation.

In the case of drugs

1. If when retailed for medicinal purposes under a name recognized in the Pharmacopoeia, it be not equal in strength or purity to the standard there laid down.

2. If when sold under a name not recognized in the Pharmacopoeia it differs materially from the standard laid down in approved works on materia medica or the professed standard under which it is sold.

However, the addition to an article of food or a drug of some foreign body or the withdrawal of an unimportant constituent for purposes of preservation, to allow of packing or transportation, or to facilitate the subsequent preparation for comsumption, cannot be considered as illegitimate, nor can the tinting of an article with a color to add to its attractiveness or for other reasons; similarly there may be allowed a reasonable proportion of matters ordinarily included during the operation of collection, transportation, or preparation for the market, or additions to inhibit the use for a certain purpose while not interfering with its nse for others, or to retain certain important properties (*e. g.*, solubility). But in all the above concessions the presence of such additions or the removal of constituents must be admitted at the time of sale unless they are so customary as to be well known to the public and expected by the purchaser, and in the case of additions to foods or drugs, that they are wholesome or innocuous.

Articles wholly factitious do not properly come under the definition of adulterants though taken cognizance of in the laws on the subject.

The extent of the practice of adulteration at the present time is undoubtedly greatly exaggerated, for the proportion of adulterated foods and beverages on the market to those unquestionably pure is far less than is popularly believed. Many products reputed to be most subject to tampering, are in reality the purest, and many of the adulterants, if not wholly imaginary, are seldom or never met with at present.

The steady decline in the practice of adulteration may be credited in part to the zeal of the civil authorities co-operating with analysts, and partly to the continuous reduction in the price of raw materials and improvements in the processes of preparation and manufacture that have lowered the cost of the

products so far that it is no longer profitable, at least on a small scale, to continue the use of adulterants formerly much cheaper than the article itself. And manufacturers and dealers not overscrupulous, have come to realize that in the long run, the profits gained in a fraudulent way do not compensate for the inevitable loss of reputation. Yet, even at the present time, it is remarkable how great ingenuity is displayed by some who devote their talents to discovering how far and in what manner adulteration can be practiced without likelihood of detection; and it is alleged that in some establishments chemists are employed chiefly for this purpose.

Where adulteration is suspected, the sampling of the article should, if possible, be done in presence of the health officer or the buyer and seller or their representatives, and the sample immediately divided into three equal parts, one for each party, and the third sealed up and reserved for an umpire. Material that is wholly or partly organic should as a rule be analyzed as soon after sampling as practicable.

It is of course a great advantage, especially in legal controversies, if the adulterant can be separated as such in a pure state and produced as evidence. Even approximate separations, yielding the adulterant in a fairly pure state, such as obtained by fractional solution, distillation, etc., may answer the purpose, provided the distinguishing properties of the adulterant are not masked by the bodies remaining associated with it.

A direct separation, however, is often impossible for the reasons that the composition of the adulterant approaches closely to that of the original, the chemical and physical properties of the two are similar, or marked chemical characteristics are wanting in one or both. These and other causes may prevent a direct separation, and so recourse must be had to attributive methods or crude mechanical separations.

A determinable chemical constituent may be normal to the original but absent from the adulterant, or vice versa, and allow a fairly accurate determination, calculating from the constituent to the compound containing it; the same is true of an associate normally present in either in a fairly constant proportion.

A certain definite change that the original or adulterant undergoes on treatment by some regeant with increase in weight or volume may be availed, or the new combination may admit of direct gravimetric or volumetric determination.

In some few instances, only the adulterant reacts directly with a volumetric solution or dissolves to a colored solution at once or after a chemical change, affording an easy and accurate estimation. The possible influence on the titration or the colorimetric comparison by the constituents of the original must be considered. The above applies as well when only the original reacts or colors the solution.

Attributive methods may be applied where a constant of the original is determinable and the same constant of the adulterant is nil, or the reverse, or where both possess the constant but in widely differing ratios. It must be remembered however that the calculated figure for a constant of two admixed bodies can be brought to equal that of either by the judicious addition of a third, hence the risk in attempting to pronounce on the genuineness of a sample from the determination of but one constant. And in cases where the constants do not differ greatly, the maximum of the lower in some varieties may reach the minimum of the higher. Obviously the more extended the examination and the greater the number of constants determined the more easily is sophistication detected, and the more confidently may the chemist pronounce on the purity of a sample.

Microscopic examination, often the easiest and surest means of detecting adulteration, may sometimes be applied as a means of numerical estimation, this when the difference in appearance between the original and adulterant is great enough to admit of a sharp distinction, or when by staining, application of polarized light, selective solvents, etc., can be brought to this condition.

Finally, it must be considered that in the more scientific modes of falsification the adulterant may not be incorporated in the form usually found on the market but only after some preliminary treatment that has modified its constitution, appearance or reactions. Hence the futility of attempting to draw conclusions from reactions valid only with the adulterant in the ordinary commercial state.

To pronounce positively on the purity of many organic commercial bodies is often difficult and it is sometimes necessary to lay down a standard of purity that is more or less arbitrary. This applies particularly where the methods are based on certain chemical or physical constants. And on account of the difficulty of isolation in the pure state, or the uncertainty attending a deduction from a set of constants, the results may be very doubtful if not altogether far from correct, and the prudent chemist will clothe his report in language that will allow a safe margin for defects in analytical methods, and not be more specific in designating the adulterant than his tests will justify.

At times one may hear applied analysis deprecated on the score that industrial analysis in general, following in the main methods that are fixed and inelastic — perhaps 'standard' — in no way aids in the development of chemistry as a science or analysis as an art, and opposes the breadth and individuality that should characterize the chemist; as evidence is cited the custom in some industries of intrusting analytical work to tyros ignorant of the significance and purpose of the operations they mechanically perform, lowering the practice to a mere subservience to a string of recipes. A few would even go so far as to exclude applied analysis from the list of intellectual arts and classify it as a handicraft pure and simple.

But in this practical age it will hardly be contended that the application of the principles of a science to the advancement of an art is in any sense "derogatory" however "unscientific" it may be. Such ideas, advanced by so small a minority, would hardly merit serious consideration were they not urged by a few whose standing in the chemical world gives weight to their opinions.

In defense of the dignity of technical analysis * it may be said that objections like these are advanced the more confidently in proportion as the critic is unfamiliar with the nature and diversity of the problems to be solved in technical analysis and the original investigation necessitated by the limited information to be gathered from the literature on special branches of technology. As to the incompetence of many employed in technical work it may be answered that the practice of engaging as assistants those with little or no chemical knowledge is undoubtedly on the wane. It is well that such is the case, although at present usually the analytical work assigned to novices is of the simplest character, and so monotonous and wearying that a trained analyst would endure it only so long as compelled by stress of circumstances. And those who are content to remain permanently at routine analysis are not of the class from which research for scientific or practical ends may be expected whatever the

* Journ. Amer. Chem. Socy. 1896—81.

position in which they may be placed. Finally it must be considered that through a steady demand for those having at least an elementary education in the principles and practice of chemistry, there is provided for others — perhaps those who most decry it — an opportunity and facilities for the prosecution of research along more congenial and less utilitarian lines.

To the student who proposes to adopt chemistry as a profession a few hints as to the opportunities of engaging in this line, the prospects of advancement, and the course of study that will aid him to success, may be helpful.

Leaving out of consideration the occupation of teaching, two courses are open for the graduate: he may establish a public laboratory, or become an employé of a manufacturing or other industry.

The outcome of a venture of the first kind is problematical. To build up a business, the essentials are a location within convenient reach of his patrons, whether his clientele is the general public or those engaged in a special line of business, an extensive personal acquaintance among those from whom he may derive patronage, and a reputation for integrity and professional ability. Attaining these, and with a fair share of enterprise, discretion and business ability, he may in time arrive at a comfortable income, or more if fortunate enough to secure large contracts. But, for the beginner, probably a long period will elapse before he can gain an adequate reputation and patronage and the experience that will enable him to advise with the client more versed in practical than scientific affairs and to whom an analysis alone, though minute and exact, will often fail to give the information he seeks.

Competition is as evident among public analysts as elsewhere, and he will be forced to recognize if not to meet, the rivalry of those who from childhood have been accustomed to habits of severe frugality and are content with an income below what the average American would consider sufficient for a bare existence, and to secure it will not hesitate to reduce their fees to a slight margin above laboratory expenses.

On the whole, unless the possession of a competency from other sources will assure independence during the first years, the outlook is not the brightest; more have failed than have succeeded.

On the other hand, should he decide to engage as a works-chemist, it is likely that he will more easily find employment in a laboratory where a number of chemists are engaged, since changes in the working force and additions are more frequent than in a smaller establishment. Points in favor of beginning in a laboratory of this kind are that experience and technical knowledge are not so essential as elsewhere, and that he can avail himself of the counsel and assistance of his older associates. If his tastes incline in the direction of the supervision of some branch of a manufactory, the opportunities for advancement to such a position are exceptionally good, as it is the policy of the administration of many works to promote chemists to be heads of departments if found to possess the requisite executive ability.

Against such a position is the monotony of the continuous grinding out of one kind of determinations, long and perhaps unseasonable hours, and a salary that may hardly exceed that of an office clerk. As a permanent engagement there is little that is attractive, yet as an antecedent to one more congenial and lucrative it has much to commend it.

In the majority of works-laboratories the number of analyses required is not sufficient to justify the employment of more than one chemist, and usually the

analytical work is more varied and interspersed with practical experiments, so that he escapes the tedium of confinement to one special kind of analysis. Being alone, the chemist must rely more on his own ability to choose and adapt methods best suited to his purposes, and has usually some time at his disposal for investigation and experiment in this direction. The opportunity for devising improvements and economies in the processes of manufacturing or in other directions is greater than in larger works provided with a scientific staff, and where study and experiment have already so far perfected the technic that no betterment seems possible short of a radical change.

Detracting from such a position is the comparative isolation of the chemist. Confined for the most part to the laboratory, he is deprived of association with others following scientific pursuits and the benefit of their counsel and encouragement and can form fewer acquaintances among those in other practical occupations and in business through whom advancement most frequently comes. Another drawback is the injunction of secrecy in regard to the details of the manufacture and innovations, restraining him from publishing and receiving credit from his fellows and the public for meritorious work he may do, granted that his discoveries are not so specific in nature as to be of no general interest.

A source of annoyance or worse that he will likely encounter will be the open or secret jealousy of some of the "practical" fellow-employees of the establishment, who fearing loss of prestige from exposure of their ignorance or errors, are ever on the alert to belittle and oppose any really advantageous step the chemist may propose, and as the advent of a laboratory is to many works a novelty whose usefulness has yet to be proved, the administration is apt to view it as a rather dubious and costly experiment and display a painful regard for economy in fitting up laboratory quarters, the purchase of supplies, and particularly toward the salary of the chemist.

Let us briefly consider the question so important to one contemplating the adoption of the practice of chemistry as a vocation, as to the course of study in general and particular that shall best fit him to assume the duties of the technical or industrial chemist.

Unquestionably the subject has not suffered for want of discussion. It has been written on and spoken on from every conceivable point of view, by those who from a long and comprehensive acquaintance with the correlation of analysis and practical affairs and the possibilities and limitations of the college and technical school are qualified to express opinions that merit earnest consideration, and by others whose knowledge of either or both is limited to vague theories gained at second-hand.

As might be supposed, the convictions of the former class differ greatly Some advocate a course confined largely or exclusively to theoretical chemistry and synthetic organic experiment, others lay stress on the desirability of a maximum of special practical work in technical analysis and the study of processes. Out of the voluminous arguments that have been advanced by the adherents of either side, let me extract from the writings of a few authors that may fairly represent the extremes.

The first is from a letter by Prof. Dr. Ostwald of Leipzig.*

"When the student [of a German university] has finished his course he is still entirely free to choose between a scientific and technical career. This is a very important point in our educational system; it is made possible by the cir-

* Chemist & Druggist, 1896—353.

cumstance that the occupation of a technical chemist in a works is very often almost as scientific in character as in a University laboratory. This is connected with a remarkable feature in the development of technical chemistry in Germany — the very point upon which the important position of chemical manufacture in this country depends. The organization of the power of invention in manufactures and on a large scale is, as far as I know, unique in the world's history, and it is the very marrow of our splendid development. Each large work has the greater part of its scientific staff — and there are often more than 100 *Doctores Phil.* in a single manufactory — occupied, not in the management of the manufacture, but in making inventions. The research laboratory in such a work is only different from one in a University by its being more splendidly and sumptuously fitted than the latter. I have heard from the business managers of such works that they have not unfrequently men who have worked for four years without practical success; but if they know them to possess ability they keep them notwithstanding, and in most cases with ultimate success sufficient to pay the expenses of the former resultless years.

It seems to me a point of the greatest importance that the conviction of the practical usefulness of a theoretical or purely scientific training is fully understood in Germany by the leaders of great manufactories. When, some years ago, I had occasion to preside at a meeting, consisting of about two-thirds practical men and one-third teachers, I was much surprised to observe the unhesitating belief of the former in the usefulness of entirely theoretical investigations. And I know a case where, quite recently, an 'extraordinary' professor of a University has been offered a very large salary to induce him to enter a works, only for the purpose of undertaking researches regarding the practical use of some scientific methods which he had been working at with considerable success. . . . You will excuse my boasting about our German management of this most important question of scientific education. It is no blind admiration without criticism, for I know by practical experience the management in other countries and I can compare them."

The second an extract from a paper by Bancroft* on the Relation of Physical Chemistry to Technical Chemistry.

" . . . To my mind, specialization and research work do not give the proper training. . . . A man specializing in organic chemistry gets a training in manipulation and in methods of making new compounds; in addition, he increases his knowledge of chemistry and of chemical phenomena. This work qualifies him to meet one of the requirements of the manufacturer; he can make himself valuable in discovering new and useful compounds, and in working out new methods of making compounds already known. His training has not been of a nature to make him especially valuable in improving methods . . . . I wish to emphasize the fact that the ideals of the organic chemist are not the ideals of the manufacturer, and that a training in organic chemistry is not the best training for a technical chemist. I have laid stress on the training in organic chemistry, rather than on the training in inorganic chemistry, because organic chemistry rather overshadows inorganic chemistry in most of our universities and colleges. It is, however, equally clear that inorganic chemistry, as now taught, does not offer the ideal training for a technical chemist. . . . . Personally, I do not believe in the teaching of technical chemistry as technical chemistry. To my mind, a comparison of German results with English results shows very conclusively that the best way to teach technical chemistry is to teach scientific chemistry. . . . . The whole matter can be summed up in a few

* Journ. Amer. Chem. Socy. 1899—1101.

words. A good training in physical chemistry is the best possible preparation for a technical chemist; . . . . "

The third, from a communication by Percy Williams, of Colorado,* writing on the subject of the technical training of metallurgical chemists.

" . . . . It is immaterial how careful, accurate and conscientious the new graduate may be; upon his advent into the mine or smelter laboratories he is simply overwhelmed by the amount and variety of his first day's work, and may be either cast adrift to hunt up another position, not feeling particularly encouraged by his first experience at practical work, or if he is particularly fortunate he may be retained at the establishment in some subordinate capacity at a small salary and given an opportunity to familiarize himself with those countless details which he was unable to acquire in his school. The opportunities, however, of taking a post-graduate course in some smelting company's laboratory while the company itself pays the tuition bills are rare, and the result is that a large percentage of our technical graduates must undergo a protracted course of hard knocks, drifting about the mining districts, receiving a smattering of valuable experience here and there until eventually they find themselves sufficiently practiced to hold a difficult position with a smelter and able to make accurately a hundred analyses every day if need be.

It is but justice to the manager to admit that he cannot be expected to spend time and money in allowing his laboratories to become a training school for young men fresh from their universities or mining schools; indeed he has the right to expect that reputable mining schools shall send him assistants fully prepared to enter upon the duties required of them and earn the salaries paid to them.

Yet all metallurgists who have been in charge of any of our large smelter laboratories for any length of time know that nine out of every ten men who enter their offices direct from school prove unsatisfactory, however great their ability and earnestness of purpose may be, because they become at once confused by the amount and variety of work which must be accomplished. They are ignorant of most of those important little details of manipulation, familiarity with which alone enables the chemist to become a rapid analyst without making any concessions to accuracy.

. . . . Some of my associates will think the picture I have attempted to draw, illustrating the difficulties besetting the path of the improperly trained chemist, to be exaggerated; but I am satisfied that the chemists themselves who have attempted to fill responsible positions directly after their graduation will agree that I have not overestimated the terrors of the situation."

The fourth, a letter from the manager of a large manufactory, to whose acumen and wide experience many can bear witness —

" . . . . As you say, I have exceptionally good opportunities for placing young men in our laboratory with a view of promoting them later on, and observe how they get on with chemical work . . . . . For some years I have refused to take on any graduate who has not had a year's practical experience, at least, in my line of work after he has graduated. The reason is that I am tired of the trouble and confusion that a beginner always causes. Not one of them, and I have had men from many of the large universities abroad and some in this country, but what was deficient in what we needed most, I mean that there was a want of a broad enough knowledge of analytical chemistry to take hold of the analysis I wanted and carry them along without constant supervision. Some were well posted in assaying, water analysis, etc., but none

* Engineering and Mining Journ., 1897 — 477.

of them had any practice in the kind of work done here [organic, principally] . . . . . So in future I shall let the 'other fellow' do the finishing up of their education and when they have spent a year or so in his laboratory they can apply to me.

Another writer* refers in the same strain to industries wherein the chemist has the direction or oversight of a department of the works —

"Some years ago a chemical firm in one of our Eastern cities was desirous of obtaining the services of a chemist who should take charge of the factory. Accordingly advertisements were inserted in the industrial journals for a man who should not only be familiar with the analytical work necessary, but who could also assume the responsibility of overseeing the plant, checking the running of the various processes, and meeting the emergencies that are constantly arising in operations of this kind.

A large number of answers were received. Interviews were requested with those who, from their letters, appeared to be the most likely to suit. But, as a result, it soon appeared that the securing of a competent man was by no means an easy matter. Some of the applicants whose letters were most assuring, turned out to have been simply laboratory boys. Others, more promising, were of foreign birth, but unfamiliar with the language and customs of their [adopted ?] country. Some were undesirable on account of their personal manner or character. But by far the most general objection was that the knowledge and experience of these chemists were limited to the field of analytical chemistry and to the work of the laboratory. They were entirely familiar with the handling of beaker glasses and funnels, platinum crucibles, analytical balances, burettes and flasks But in the matter of treating material in large quantities, and obtaining results in the factory, they came up, as it were, against a stone wall. Many of them, in fact, were literally as unfamiliar with the operations of a chemical plant as they were with the working of an astronomical observatory."

"It should be observed that the case here described is by no means an isolated one. There is reason to believe that there is hardly a large chemical manufacturer in the country who, at one time or another in his life, has not had experiences of a nature similar to this one."

"It will be admitted that the question of technical education is a most important one. It deserves at least as much attention in the United States as it does elsewhere, on account of the remarkable progress and development of industrial activity here . . . . . It is for this important field, then, that the universities and technological schools of the country prepare their young men. And it is because the quality of this technical talent is so frequently below what is called for that I venture to draw attention to certain considerations on the subject that may be of interest . . . ."

Between such diametrically opposite views as are held by those who have just been quoted all shades of opinion prevail, and it is not likely that any agreement can be reached, however far the discussion may be extended. It will be noted however that each writer on the subject has in view a particular industry or class of industries for which he opines the technical chemist should be specially trained.

Let me present a few observations that seem germane to the subject.

The views of those who favor a course of instruction mainly or exclusively confined to theory and original investigation in organic and physical chemistry have in most cases been formed through a study of the conditions of manufacture and trade prevailing in foreign countries. In America the situation presents many and obvious differences.

* The Leather Manufacturer, 5—2.

The manufacturers of this country, with of course some notable exceptions, as a class are not so inclined to devote their highest efforts to attaining and maintaining an unexcelled and, if possible, an unrivaled quality in their wares. A large output immediately marketed, offers such financial inducements that many are quite indifferent whether the product of competitors equals or surpasses their own, so long as a satisfactory profit is forthcoming. Until recent years, also, competition has not been so keen as to reduce the margin of profit to a point where strict attention to the minor economies of manufacture and the utilization of waste products becomes a necessity.

Again, many of the great industries of Europe have their counterparts here only in a small way, if at all — we have no Merck, no Baeyer, no Analin Fabrik that can absorb hundreds of graduates in employment in research work along lines almost identical with their exercises in the universities. American establishments of this kind are smaller and less independent financially, and their products fewer and more limited to the staple articles in common use. And the general policy of the manufacturer is rather in the direction of lowering the cost of manufacture of his products by high organization of labor, the installment of labor-saving machinery, and greater rapidity of conversion, than toward the discovery and invention of new processes and products.

Finally, it cannot be denied that in America science and its followers are not accorded that universal respect that is so plainly noticeable in European countries. From various causes, there is here a disposition among the so-called practical men to disparage or deride the efforts of those who would bring scientific principles and manufacturing practice into harmonious association, and the depreciation of such, expressed with characteristic positiveness, will oftentimes be more convincing to the uninformed than the moderate assertions of the more liberal and well-informed.

The chemical course of the scientific school aims to combine a training in chemistry and allied subjects with, as far as may be, a preparation for practical work in technical laboratories, in addition to such other studies as it is believed will conduce to a broad and liberal mental training. The four years course pursued at the leading scientific schools is made up usually on the following lines. During the Freshman year general chemistry is the major study, with mathematics, a foreign language, and elementary physics as minors; in the second year these subjects are continued and inorganic qualitative analysis begun. Inorganic quantitative analysis is the main requirement during the Junior year, with exercises in the gravimetric and volumetric determinations of the common metals, electrolytic assays, and gas analysis. In the Senior year are taken up technical and manufacturing chemistry, metallurgy, and technical analysis, with more or less synthetical organic work including ultimate organic analysis — the latter forming the greater part of the year's employment in some institutions. The practice in technical analysis is usually in the line of examinations of iron and steel, ores, waters, foods, and dairy products.

A comprehensive acquaintance with general chemistry is indispensable to the progressive technical chemist in whatever line of technical work he may be engaged. For so intimate is the connection between the principles there enunciated and illustrated and the practice of analysis and technology that one not well grounded therein must necessarily be mechanical in whatever he essays, lacking the confidence to leave the beaten path of detailed methods and practice.

Qualitative analysis acquaints the student with the properties of the common elements and their chemical reactions and affords practice in many

of the manipulations used in quantitative analysis, and as such is the logical introduction to the latter. Of late years the tendency is to shorten the time devoted to qualitative work to the benefit of quantitative, which is without doubt a move in the right direction, considering how short a time at best can be allowed the latter. For some rather obscure reason instruction in qualitative analysis has usually been confined to the common metals and acids to the exclusion of organic bodies to which a considerable part of the course might be devoted with advantage.

The allied branches — physics, mineralogy, metallurgy, electro-chemistry, pharmaceutics, etc., all contribute in some degree to the attainments of the student and prove of special practical use in future life.

Applied chemistry, describing the application of chemical principles to manufacturing and the arts, is of value in disclosing the possibilities in manufacturing processes and drawing attention to the prime consideration of every process, that of cost of installation and prosecution. Especial attention should be paid to the modern practices that have almost revolutionized many industries, and to comparison with those antiquated and obsolete.

As an auxiliary study I would strongly recommend the *details of technology*, meaning by this the particulars of the preparation, application and use of the different varieties of such materials as are common to all manufacturing establishments. However well instructed in chemistry and general technology the graduate may be, it is hardly probable that on entering the laboratory of a manufactory he will be able to suggest any important changes in the routine of manufacture or will have gained the confidence of the management to the extent that it will entertain on his advice alone any proposition involving the expenditure of a considerable sum or any radical modification of a process. Many chemists who have attempted to introduce material changes before gaining a thorough acquaintance with the processes involved have met only failure and derision.

But in every manufactory there are a large number of minor matters that may well engage the attention of the young chemist, points where there has been no investigation heretofore or at least none sufficiently thorough. He will doubtless find that there are in use many materials that while answering their respective purposes fairly well can often be improved on or replaced by something better or cheaper; or the grade of purchases may be variable, sometimes up to standard, sometimes below.

Such, for example, are paints for special localities exposed to the weather, gases, or gritty dust; the coal for steam generating, the water used for boilers or cleansing and its purification if necessary; the lubricants for variously weighted journals; iron and brass castings; antifriction metals; illuminating oils; waste and packing, etc. The examination of such articles and the endeavor to correct their faults or replace with something better cannot fail to result in an aggregate improvement or saving that will alone repay the cost of the laboratory and the salary of the chemist. One who is alert and studious can always find sufficient subjects for investigation to profitably occupy a large share of his time while incidentally gaining that intimate knowledge of the principles and practice of the routine of manufacture that will restrain him from proposing or assenting to changes that are impracticable or useless.

During the first years of practical life the chemist should endeavor to master the business principles that govern every successful industrial plant even though he should have no expectation of entering a position where he would be called on to apply them. For as in the discussion of matters appertaining to

his engagement, he is brought into personal contact with those in authority, their estimate of his ability and value in his position will often be formed more in proportion to his familiarity with practical affairs than from his strictly scientific attainments however great. And this is also true of others with whom he may have business relations. Even so small an accomplishment as the ability to use the customary trade-names when speaking of tools and the details of machinery will gain for him a certain respect among workmen that is desirable when he would seek their advice or co-operation, often most valuable.

Up to recent years a student had necessarily to prepare himself, as far as possible, for every line of chemical work. For of the industries of this country commonly employing chemists, in but two or three were the plants so numerous and extensive as to warrant one in confining his studies and exercises in analysis and technology to the class of work there pursued, with a reasonable expectation of obtaining employment therein. Moreover, in these industries a permanent position is less certain than in others, the one peculiarly susceptible to the fluctuations of the market, responding to the earliest hint of a general business depression by curtailing or ceasing operations for an indefinite period; the other liable at any time to face the exhaustion of its natural supplies. One who was so fortunate as to know in advance in what particular line of industry he would be employed and the nature of the analytical and other work he was to undertake, had of course no difficulty in arranging the latter part of his educational course along the same lines. But the majority of students had no such assurance, and after graduation cast about for employment and accepted what offered. With this prospect in view he has had to consider what studies afforded the best training in the way of enabling him to enter wherever opportunity offered with a fair promise of a successful career.

But with the advent of a more rational scientific operation of manufacturing plants, the generally admitted value of chemical analysis to the buyer of materials, and the substantial interest manifested in the application of chemistry to the arts, the field open to the chemist has widened until he can now prepare for a single department with reasonable assurance of finding employment therein.

It may be conceded that no course of study of the usual collegiate length can possibly constitute an adequate preparation for the immense variety of analytical work that is demanded in the different industries the graduate may enter. It is impossible for even the most gifted and industrious to become an expert in assaying ores, analyzing iron and steel, dyestuffs, fertilizers, drugs and pharmaceuticals, dairy products, explosives, oils, and the long list of other materials, each class demanding considerable special practice ere confidence in the analytical results is obtained. It matters little how expert the chemist may be in one line, the difficulties he encounters in essaying another can only be surmounted by special study and practice — the less, of course, in proportion as the general principles of analysis have been mastered and dexterity in manipulation acquired.

Formerly, the student had little voice in the selection of the studies that should comprise a chemical course; a single rigid routine was insisted on, regardless of the purposes and prospects of the student, and optional branches were few. Latterly, a more liberal policy obtains in the more progressive schools; who, while insisting on the pursuance of a combination of studies that is designed to give breadth and mental culture, yet allow more or less change by the substitution of special branches, and where a degree in course is not to

be conferred, offer special courses adapted to qualify the student for engaging in any special industry he may elect. In making such a selection, the experience and foresight of those who have arranged the courses should be given due consideration, and their advice regarding the curtailing or omission of certain studies and the substitution of others should be sought before a decision is made.

Finally, there can be no doubt that in future a more thorough grounding in technical analysis will be required of the industrial chemist than has been the rule in the past. The complaint of Williams as to the inability of the recent graduates of technical schools to cope with the routine work of the smelter laboratory is no doubt well founded. Much the same condition has prevailed—and still is in evidence to some extent—in iron and steel laboratories, and those in charge of various other industries have assured me that the same is true within their observation, and that his strictures voice the prevailing sentiment among manufacturers in general.

Nevertheless while it is reasonable that an employer may insist that an applicant for the position of chemist shall be acquainted with the general principles of chemical processes and the analysis of the materials treated, and cannot be censured for engaging a chemist, as he would any other employé, on the presumption that he is master of his trade and prepared to immediately render an equivalent for his wage, he cannot in fairness expect a familiarity with the minutiae and special practice of the laboratory of a particular plant nor with analyses that involve unusual manipulations or in which a knowledge of the properties of uncommon organic compounds is essential to their determination. In no two works are the materials to be analyzed exactly the same; the methods of analysis that are deemed most suitable differ more or less; the apparatus provided varies in construction—these and other important matters may be so unlike as to confuse and discourage the beginner and embarrass for a time even one of long experience. A reasonable time should be allowed the chemist to become acquainted with his surroundings and the special routine required, and it should not be expected that a recent graduate shall be so well trained in any given line as to be capable of immediately performing as great an amount of analytical work as one with months or years of special practice.

There are many manufacturers and dealers in crude and factored articles to whom the utility of the laboratory has yet to be demonstrated. To the more progressive the advantage is already manifest, ultimately all will admit it, but it is undeniable that progress in this direction has been far slower than could reasonably be expected. The delay may be traced partly to the caution and conservatism of the proprietors who view the project as a somewhat costly and doubtful experiment; but it is undeniable that much of this hesitation is the outcome of the failures of pioneer chemists, unequal to the duties of their positions and ignorant of the principles governing the operation of a successful manufacturing plant.

All will concede that a course of instruction devoted largely or entirely to theoretical chemistry and work in organic synthesis is not to be undervalued for the knowledge and mental discipline it affords, nor is this less true where physical chemistry is the main topic. But where an education must be to a great extent a means to an end, where one must step from the college door into the technical laboratory, the inadequacy of such a course of training is apparent to all familiar with the duties of the technical chemist.

I would emphasize this point, recalling a score of failures that have come under my observation; graduates of universities of high repute at home and abroad, men of undoubted ability and well grounded in theoretical and

organic chemistry make up a good share of the list. Entering a works-laboratory where all is severely practical, he has been confronted by a first installment or an accumulation of material to be analyzed formidable enough even to one of long experience. Often mixtures of divers kinds were compounded by the manager or samples selected that had been previously examined by experts, these to be analyzed at once and the results to closely tally with the synthesis or previous analyses. Is it to be wondered at that, distrustful of what ability he really possessed, the chemist has resigned forthwith, seeing the futility of attempting the task before him, or a little later is dismissed as incompetent; and discouraged and disheartened, has abandoned further attempts and turned to a pursuit less fraught with difficulties to the beginner?

And what is more to be deplored, the failure of his initial effort cannot but raise a doubt on the part of the administration as to the advantage of chemical investigation and control to the manufacturer, especially if the laboratory is an innovation, and it is not probable that the experiment, successful only in engendering the disappointment of the managers and the derision of the workmen, will be repeated, at least until a change of administration; nor will it encourage the institution of laboratories in other works of the same or a similar kind.

It is true that those exceptionally gifted with perseverance and self-confidence will overcome these difficulties and ultimately succeed, and others from the favoring circumstances of entering large laboratories as assistants and at first assigned simple routine work, or through the lenience of employers are able to conceal their incompetency for the time being. But many times will these have cause to feel and regret the handicap of unfamiliarity with matters directly touching their employment.

The opportunities for engaging in technical and industrial chemistry are at the present time fully as great as in any other profession. Industries already more or less under chemical control are increasing their chemical staffs, and others only await the coming of those able to demonstrate the value of the art to their special practice. The field is wide and by no means overcrowded.

But the preparation of the applicant must be adequate and appropriate to the specific task he is to assume. No mere smattering of the principles and practice will suffice. Equipped with a broad and comprehensive acquaintance with technical analysis and its applications in general and a specific branch in particular, and with a fair share of self-confidence and tact, he may enter his chosen line of technical analysis with a reasonable expectation of immediate success — without these qualifications his career will likely be short and disappointing or at best bestrewn with formidable difficulties.

And with the extension of chemical control directed by those whose training has been both broad and specific there will result a better appreciation on the part of employers of the dignity and value of the art and its followers; more intimate business relations between them and the chemist will be established without the intervention of minor officials who so often restrict and hamper the successful operation of the laboratory through their inability to appreciate its scope and possibilities. On the other hand the occupation of the chemist will be less in the direction of routine work of the laboratory, the minutiae of analyses, and the search for petty economies of time and material, and more in researches and experiment in the application of chemistry to manufacturing and trade.

TABLES.

TABLE OF ATOMIC WEIGHTS.

Oxygen = 16.

Aluminum	Al	27.1	Neodymium	Ne	143.6
Antimony	Sb	120.4	Neon	No	19.94
Argon	Ar	39.92	Nickel	Ni	58.7
Arsenic	As	75.0	Nitrogen	N	14.04
Barium	Ba	137.4	Osmium	Os	191.0
Bismuth	Bi	208.1	Oxygen	O	16.0
Boron	Bo	11.0	Palladium	Pd	107.0
Bromine	Br	79.95	Phosphorus	P	31.0
Cadmium	Cd	112.4	Platinum	Pt	194.9
Caesium	Cs	132.9	Potassium	K	39.11
Calcium	Ca	40.1	Praseodymium	Pr	140.5
Carbon	C	12.0	Rhodium	Rh	103.0
Cerium	Ce	139.0	Rubidium	Rb	85.4
Chlorine	Cl	35.45	Ruthenium	Ru	101.7
Chromium	Cr	52.1	Samarium	Sm	150.3
Cobalt	Co	59.0	Scandium	Sc	44.1
Columbium	Cb	93.7	Selenium	Se	79.2
Copper	Cu	63.6	Silicon	Si	28.4
Erbium	Er	166.0	Silver	Ag	107.92
Fluorine	Fl	19.05	Sodium	Na	23.05
Gadolinium	Gd	156.0	Strontium	Sr	87.6
Gallium	Ga	70.0	Sulfur	S	32.07
Germanium	Ge	72.5	Tantalum	Ta	182.8
Glucinum	Gl	9.1	Tellurium	Te	127.5
Gold	Au	197.2	Terbium	Tb	160.0
Helium	He	3.96	Thallium	Tl	204.15
Hydrogen	H	1.008	Thorium	Th	232.6
Indium	In	114.0	Thulium	Tu	170.7
Iodine	I	126.85	Tin	Sn	119.0
Iridium	Ir	193.1	Titanium	Ti	48.15
Iron	Fe	56.0	Tungsten	W	184.0
Krypton	Kr.	81.7	Uranium	U	239.6
Lanthanum	La	138.6	Vanadium	V	51.4
Lead	Pb	206.92	Xenon	X	128.0
Lithium	Li	7.03	Ytterbium	Yb	173.2
Magnesium	Mg	24.3	Yttrium	Yt	89.0
Manganese	Mn	55.0	Zinc	Zn	65.4
Mercury	Hg	200.0	Zirconium	Zr	90.4
Molybdenum	Mo	96.0			

TABLE 2.

Metric and English Weights and Measures.

1. Standard of length, the *Meter* = 1.09361 yards. One foot = .3048 meter. One centimeter = .39371 inch. One inch = 2.54 centimeters. One millimeter = .039371 inch. One inch = 25.40 millimeters.

2. Standard of surface, the *Square Meter* = 10.764 square feet. One square foot = .0929 square meter. One square centimeter = .155 square inch. One square inch = 6.4513 square centimeters.

3. Standard of capacity, the *Cubic Meter* = 35.316 cubic feet. One cubic foot = .02832 cubic meter. One cubic centimeter = .06103 cubic inch. One cubic inch = 16.383 cubic centimeters. One liter = 1000 cubic centimeters = 1.0567 wine quarts = 33.84 fluid ounces Apoth. One cubic centimeter = .03382 fluid ounce Apoth. One gallon (U. S.) = 3.785 liters. One quart (U. S.) = 946.5 cubic centimeters. One fluid ounce Apoth. = 29.57 cubic centimeters. One fluid drachm Apoth. = 3.696 cubic centimeters.

4. Standard of weight, the *Gram* = 15.432 Troy grains = .2572 Apoth. drachm = .03527 Avoirdupois ounce = .03215 Troy ounce. One kilogram = 2.205 Avoirdupois pounds = 2.6792 Troy pounds. One Troy grain = .064799 gram. One Troy drachm = 3.887 grams. One Troy ounce = 31.10 grams. One Avoirdupois pound = 453.55 grams. One Troy pound = 373.22 grams. One Avoirdupois ounce = 28.35 grams.

One Avoir. oz. = .91146 Troy oz. One Troy oz. = 1.09714 Avoir. ozs.

One Avoir. lb. = 1.21528 Troy lbs. One Troy lb. = .82286 Avoir. lb.

Prefixes in the metric system. Deka-, ten; Hecto-, one hundred; Kilo-, one thousand; Deci-, one-tenth; Centi-, one-hundredth; Milli-, one-thousandth. These apply to all the standards.

TABLE 3.

Weight in Grams of 1000 Cc. of Gas at Zero Cent. and 760 Mm. of Mercury.

Hydrogen	.0896	Nitrogen protoxide	1.9745
Methane	.7190	Carbon dioxide	1.9772
Ammonia	.7707	Alcohol	2.0862
Water	.8063	Cyanogen	2.3360
Acetylene	1.1650	Sulfur	2.8430
Ethylene	1.2510	Sulfur dioxide	2.8689
Carbon monoxide	1.2513	Chlorine	3.1801
Nitrogen	1.2562	Ether	3.3170
Air	1.2939	Chloroform	4.4507
Ethane	1.3404	Bromine	6.8697
Oxygen	1.4298	Mercury	9.0210
Hydrochloric acid	1.6131	Iodine	11.2710

TABLE 4.

Volume and Density of Water at Different Temperatures.

(Rossetti).

Temp. °C.	Volume of Water (at 0° = 1).	Sp. Gr. of Water (at 0° = 1).	Temp. °C.	Volume of Water (at 0° = 1).	Sp. Gr. of Water (at 0° = 1).
0	1.00000	1.000000	19	1.00141	0.998588
1	0.99994	1.000057	20	1.00161	0.998388
2	0.99990	1.000098	21	1.00183	0.998176
3	0.99988	1.000120	22	1.00205	0.997956
4	0.99987	1.000129	23	1.00228	0.997730
5	0.99988	1.000119	24	1.00251	0.997495
6	0.99990	1.000099	25	1.00276	0.997249
7	0.99994	1.000062	26	1.00301	0.996994
8	0.99999	1.000015	27	1.00328	0.996732
9	1.00005	0.999953	28	1.00355	0.996460
10	1.00012	0.999876	29	1.00383	0.996179
11	1.00022	0.999784	30	1.00412	0.99589
12	1.00032	0.999678	40	1.00757	.....
13	1.00044	0.999559	50	1.01182	.....
14	1.00057	0.999429	60	1.01678	.....
15	1.00071	0.999289	70	1.02243	.....
16	1.00087	0.999131	80	1.02874	.....
17	1.00103	0.998970	90	1.03554	.....
18	1.00122	0.998782	100	1.04299	.....

TABLE 5.

Formulae for Converting the Reading of One Thermometer to Another.

Fahrenheit to Centigrade, subtract 32 and multiply by .5556.
Centigrade to Fahrenheit, multiply by 1.8 and add 32.
Fahrenheit to Reaumur, subtract 32 and multiply by .4444.
Reaumur to Fahrenheit, multiply by 2.25 and add 32.
Centigrade to Reaumur, multiply by .8.
Reaumur to Centigrade, multiply by 1.25.

Degrees Centigrade Corresponding to Degrees Fahrenheit.

Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.
50	10.0	60	15.6	70	21.1	80	26.7	90	32.2
51	10.6	61	16.1	71	21.7	81	27.2	91	32.8
52	11.1	62	16.7	72	22.2	82	27.8	92	33.3
53	11.7	63	17.2	73	22.8	83	28.3	93	33.9
54	12.2	64	17.8	74	23.3	84	28.9	94	34.4
55	12.8	65	18.3	75	23.9	85	29.4	95	35.0
56	13.3	66	18.9	76	24.4	86	30.0	96	35.6
57	13.9	67	19.4	77	25.0	87	30.6	97	36.1
58	14.4	68	20.0	78	25.6	88	31.1	98	36.7
59	15.0	69	20.6	79	26.1	89	31.7	99	37.2

TABLE 6.

Corresponding Heights of the Barometer in Millimeters and Inches.

Mm.	Inches.	Mm.	Inches.	Mm.	Inches.	Mm.	Inches.	Mm.	Inches.
730	28.74	740	29.13	750	29.53	760	29.92	770	30.32
731	.78	741	.17	751	.57	761	.96	771	.36
732	.82	742	.21	752	.61	762	30.00	772	.39
733	.86	743	.25	753	.65	763	.04	773	.43
734	.90	744	.29	754	.69	764	.08	774	.47
735	.94	745	.33	755	.73	765	.12	775	.51
736	.98	746	.37	756	.76	766	.16	776	.55
737	29.02	747	.41	757	.80	767	.20	777	.59
738	.06	748	.45	758	.84	768	.24	778	.63
739	.10	749	.49	759	.88	769	.28	779	.67

TABLE 7.

Equivalent of the Fraction $\frac{.0012562}{760\ (1 + .00367t)}$ (page 247).

Tem.	Equivalent	Tem.	Equivalent	Tem.	Equivalent
15	.0000015667	21	.0000015846	27	.0000015039
16	.0000015612	22	.0000015294	28	.0000014989
17	.0000015558	23	.0000015242	29	.0000014939
18	.0000015505	24	.0000015191	30	.0000014890
19	.0000015452	25	.0000015140	31	.0000014841
20	.0000015399	26	.0000015089	32	.0000014792

TABLE 8.

Tension of Aqueous Vapor in Millimeters of Mercury.

° Cent.	Mm.	° Cent.	Mm.	° Cent.	Mm.	° Cent.	Mm.	° Cent.	Mm.
10.	9.16	15.	12.70	20.	17.39	25.	23.55	30.	31.55
10.5	9.47	15.5	13.11	20.5	17.94	25.5	24.26	30.5	32.46
11.	9.79	16.	13.54	21.	18.50	26.	24.99	31.	33.41
11.5	10.12	16.5	13.97	21.5	19.07	26.5	25.74	31.5	34.37
12.	10.46	17.	14.42	22.	19.66	27.	26.51	32.	35.36
12.5	10.80	17.5	14.88	22.5	20.27	27.5	27.29	32.5	36.37
13.	11.16	18.	15.36	23.	20.89	28.	28.10	33.	37.41
13.5	11.53	18.5	15.85	23.5	21.53	28.5	28.93	33.5	38.47
14.	11.91	19.	16.35	24.	22.18	29.	29.78	34.	39.57
14.5	12.30	19.5	16.86	24.5	22.86	29.5	30.65	34.5	40.68

TABLE 9.

EMPIRICAL VOLUMETRIC SOLUTIONS.

Let it be required to make up of a reagent *a* a solution of which one cubic centimeter shall react with *b* grams of an element or compound *c*; then $b \times F$ is the theoretical weight in grams of *a* to be dissolved to one liter.

a	*c*	*F*
Arsenious oxide	Iodine	390.2
" "	Chlorine	1396.3
Barium chloride cryst.	Sulfuric acid (H_2SO_4)	2491.0
Barium hydrate cryst.	Nitric acid (HNO_3)	2502.4
" " "	Hydrochloric acid	4827.5
" " "	Carbon dioxide	7172.5
Ferrous sulfate cryst.	Potassium permanganate	8797.1
Hydrochloric acid	Sodium carbonate, anhydrous	687.2
" "	Potassium carbonate	527.5
" "	Potassium hydrate	649.7
" "	Sodium hydrate	910.1
" "	Nitrogen (as ammonia)	2596.7
" "	Ammonia (NH_3)	2136.5
Iodine	Sodium thiosulfate anhydrous	801.6
"	" " crystallized	510.8
"	Hydrogen sulfide	7442.9
"	Sulfur dioxide	3959.7
"	Arsenious oxide	2562.6
"	Tin (as stannous chloride)	2131.9
Iron (as ferrous salt)	Nitric acid (HNO_3)	2664.7
" " " "	Manganese dioxide	1287.4
" " " "	Potassium permanganate	1770.9
" " " "	Potassium bichromate	1141.2
" " " "	Chromium trioxide	1678.3
Oxalic acid cryst.	Potassium hydrate	1123.1
" " "	Manganese dioxide	1448.8
" " "	Sodium hydrate	1573.3
" " "	Ammonia (NH_3)	3693.4
" " "	Nitrogen (as ammonia)	4488.9
Potassium permanganate	Iron (as ferrous salt)	564.7
" "	Hydrogen peroxide	1859.2
" "	Oxalic acid ($H_2C_2O_4$)	702.6
" "	Oxalic radical (C_2O_4)	718.7
" "	Manganese (by precipitation)	1916.5
" "	Nitrous acid (HNO_2)	1844.2
" "	Calcium oxide (as oxalate)	1127.3
" "	Molybdenum sesquioxide	790.6
" "	Potassium ferrocyanide, anhyd.	85.8
Potassium hydrate	Sulfuric acid (H_2SO_4)	1144.3
" "	Hydrochloric acid	1539.3
" "	Nitric acid (HNO_3)	890.1
" "	Acetic acid ($HC_2H_3O_2$)	934.8
Potassium bichromate	Iron	876.2
" "	Lead	711.4
" "	Potassium iodide	295.7
" "	Glycerol	7462.0
Potassium chromate	Barium	1414.3

Potassium chromate	Lead	939.1
Potassium iodide	Iron	2963.6
" "	Copper	5218.9
" "	Chlorine	4681.5
" "	Bromine	2075.8
Potassium cyanide	Copper	4097.5
Potassium sulfocyanide	Silver	900.9
" "	Copper (cuprous)	1528.6
Silver nitrate	Chlorine	4794.3
" "	Bromine	2125.8
" "	Iodine	1339.9
Sodium carbonate, anhyd	Hydrochloric acid	1455.1
" " "	Sulfuric acid (H_2SO_4)	1081.7
" " "	Nitric acid (HNO_3)	841.4
Sodium chloride	Silver	542.1
Sodium thiosulfate cryst	Iodine	1957.6
" " "	Chlorine	7004.8
" " "	Bromine	3105.9
Sodium sulfide (Na_2S)	Copper	1229.1
" " "	Lead	377.8
" " "	Zinc	1195.3
Sulfuric acid (H_2SO_4)	Potassium hydrate	873.9
" " "	Ammonia (NH_3)	2874.0
" " "	Sodium hydrate	1224.3
" " "	Lead	474.0
" " "	Barium	713.8
Stannous chloride	Iron (as ferric salt)	1695.5

Conversely, if the concentration n of a solution of a is known, the value of b is $\frac{n}{F}$. And if the titre of a solution of a is that one cubic centimeter is equal to b gram of an element or compound c, the strength against another reacting element or compound c' may be calculated—let f and f' be the numbers in column F corresponding to c and c', then $\frac{bf}{f'}$ grams of c' reacting with the solution of a.

To make up a solution of a definite oxidizing or reducing power in terms of oxygen, that is, of a reagent a whose solution shall contain b grams of oxygen or its equivalent in one cubic centimeter, or if a reducer, one cubic centimeter shall combine with b grams of oxygen or its equivalent. The weight of a to be dissolved to one liter is $b \times F$.

Barium peroxide (with H_2SO_4)	Available oxygen	10587.5
Chromium trioxide	" "	4170.8
Hydrogen peroxide	" "	2126.0
Potassium chlorate	" "	2553.3
Potassium permanganate	" "	3952.8
Potassium bichromate	" "	6133.8
Potassium chromate	" "	8096.7
Sodium peroxide	" "	4881.2
Bromine	Equivalent to oxygen	9993.7
Chlorine	" "	4431.3
Iodine	" "	15856.2

Iron (in ferric salts)	Equivalent to oxygen	7000.0
Mercuric chloride	" "	33862.5
Ammonium oxalate cryst	Combines with oxygen	8885.0
Ferrous sulfate cryst	" " "	34772.7
Iron (in ferrous salts)	" " "	7000.0
Oxalic acid cryst	" " "	7878.0
Potassium ferrocyanide cryst	" " "	52841.0
Potassium nitrate	" " "	5321.9
Sodium sulfate cryst	" " "	15767.6
Sulfurous acid (SO_2)	" " "	4004.4
Tin (as stannous chloride)	" " "	7487.5

INDEX.

Acetic acid 225
Acetone in urine 505
Acetylation 315
Acetyl value, oils 456
Acidimetry 221
Acid value, oils 45
Acid, standard 222
Aconite, analysis 418
Adjusting balance 37
Adhesion 170
Adulteration 578
Air, analysis 245
Air-bath 25
Air-pump, water 102
Agate mortar 23
Albumin in urine 501
Alcohol 213
Alcohol, determination 393
Alcohol, reagent 206
Alcohol, methyl 396
Alcohol, amyl 397
Alkali, standard 222
Alkalies, determination 252
Alkalimeter 12
Alkaloids 409
Alkaloids, table of 409
Alkaloids, extraction 411
Alkaloids, indicators 418
Alizarin 511
Alumina in ores 355
Alumina in silicates 252
Ammonium salts, reagents 207
Ammonium sulfate 245, 553
Analytical balance 29
Analysis, accuracy 526
Analysis, colorimetric 259
Analysis, volumetric 110
Apparatus, extraction 78
Apparatus, gasometric 139
Apparatus, percolation 52
Aqueous vapor, tension 183, 594
Arsenic in iron 348
Arsenic in ores 356
Asbestos filter 91
Ash, filter 104
Ash, determination 105
Assay balance 33
Assay, fire 268
Assay weights 41
Atomic weights, accuracy 526, 545
Atomic weights, table 592
Attributive methods 155, 542
Attributive methods, physical 155
Attributive methods, chemical 171

Back titration 130
Balance, assay 33
Balance, analytical 29
Balance, equation of 34
Balance, testing 41
Barium chloride 238, 207
Barium sulfate, occlusion 532
Barium hydroxide, reagent 207
Base metals, assay 275
Batteries 279
Battery fluid, electropion 207
Beakers 49
Beeswax 466
Berberine 227
Blank analysis 9
Blast lamp 102
Bomb, calorimetric 300
Bleaching powder 325
Boat 298
Blowpipe assay 274
Blyths digester 51
Bromine, reagent 208
Bruehls apparatus 68
Bucking board 23
Bunsen burner 58
Bunsen pump 93
Buntes burette 147
Burettes 111
Burette stand 114
Burning filters 104
Butter 486
Butter adulterations 488

Camera 260
Caffeine 228
Calcium carbonate, reag 208
Calculation 174

Capillarity 168
Carbon determination..... 295
Carbon in iron 344, 347
Carbonates, analysis..... 12
Carbohydrates 427
Carbonic acid in water..... 368
Carius method 307
Carmichael filter..... 94
Casseroles..... 60
Cellulose..... 448
Centrifugal machine..... 86
Chlorate determination..... 229
Chloroform, reagent..... 208
Chlorimetry..... 322
Chloral 223
Chlorine determination 239
Chloroplatinic acid, reag..... 208
Chrome yellow..... 231
Chromic acid, oxidation..... 302
Chromometer 263, 265
Cinchona analysis..... 418
Coal 359
Coffee 217
Color phenomena..... 537
Colorimetry 259
Colorimeters..... 263
Colorimetric methods..... 536
Coal gas..... 152
Co-precipitation 96, 531
Combustion furnace..... 296
Computations 174
Condenser 63
Continuous percolation..... 52
Congealing point..... 163
Copper determination.....249, 348
Creatinin 504
Crucibles, clay..... 269
Crucibles, Gooch..... 92
Crucibles, platinum..... 100
Crucibles, porcelain..... 101
Crusher, ore..... 22
Crucible fusion..... 268
Cryoscopy..... 491
Crystallization, fract..... 83
Crystallizing dishes..... 60
Cupellation 272

Decantation..... 86
Densimetric methods..... 186
Desiccator 26
Determination, blank..... 9
Determination, parallel..... 9
Dialysis..... 84
Difference, analysis by..... 555
Diamond mortar..... 21
Dishes, evaporating..... 60
Distillation 62
Distillation, destructive..... 65
Distillation, fractional..... 65
Distillation in vacuo..... 64
Distilled water..... 211
Double filters..... 95
Drugs, extraction 411
Drying 25
Drying filters..... 100
Duclaux method..... 320
Dyestuffs 506
Dye-test..... 507

Eau de Javelle..... 327
Electrolysis..... 278
Electrodes 282
Elementary organic anal..... 295
Emmerlings tube..... 56
Empirical solutions..... 182
Empirical solutions, table..... 595
Elaidin test..... 455
End point, titration..... 117
Erlenmeyer flasks..... 49
Erdmanns float 113
Errors in analysis.....190, 544
Ether..... 220
Ether value 457
Eudiometer..... 139
Evaporation..... 57
Evaporating dishes..... 60
Evaporation in vacuo..... 60
Exercises..... 213
Extraction apparatus..... 52
Extracted filtered paper..... 89
Extraction of liquids..... 78
Extractive, malt..... 445

Fats..... 452
Fat in milk..... 479
Fehlings solution 430
Ferrous sulfate 208, 215
Fertilizers 382
Fibers, mixed, analysis..... 450
Filtration..... 89
Filtration, rapid..... 93
Filtration, liquids..... 95
Filter paper..... 89
Filter stand 90
Filter pump..... 93
Filter ash.....89, 104

Filters, burning 103
Filters, weighed..... 100
Fire assay..... 268
Fixed carbon..... 360
Flash point..... 170
Flash point, oils 462
Flasks..... 49
Flasks, volumetric..... 117
Float..... 113
Fluxing 55
Forge scale..... 230
Formulæ calculation..... 177
Fractional distillation..... 65
Fractional solution 75
Fractional precipitation..... 83
Funnels..... 90
Furfurol..... 434
Fusion of silicates..... 255
Fusel oil..... 393

Galena 237
Gas analysis 139
Gas balance..... 145
Gas, reduction to normal..... 183
Gas generators..... 72
Gases in solids..... 150
Gas pipette..... 140
Gas volumes, calculation..... 183
Gases, weight of..... 593
Gasoline gas burners..... 58
Gelatin, absorption of tannin..... 424
Ginger 218
Glass, chemical 61
Glass, dissolved 61
Glass mortars 23
Glucose 439
Glycerol..... 405
Glycerol in wine..... 407
Gold assay..... 274
Goetz tube.....15, 340
Gooch crucible..... 92
Graduated glassware..... 110
Graphite in iron 347
Gravimetric analysis..... 9
Gravimetric methods..... 529
Greiners burette 113
Grinding machines..... 23
Guarana 227

Halogen absorption..... 455
Halogen determination..... 307
Hardness of water..... 372
Heating in tubes 50
Hempels desiccator..... 26
Hide powder..... 423
Hogarths flask..... 160
Hot filtration..... 90
Hot plate..... 57
Hydrastis 227
Hydrochloric acid, reag..... 208
Hydrogen peroxide, reag..... 209
Hydrogen sulfide apparatus..... 72
Hydrometer 159
Hygroscopic bodies, weighing.... 46

Ignition 100
Ignition in gas..... 107
Igniting precipitates 102
Illuminating gas, analysis..... 152
Illuminating oils, analysis..... 461
Impurities in precipitates..... 108
Indicators 120
Indirect analysis 12
Indigo 513
Indigo, artificial..... 514
Inversion of sugar..... 434
Iron, analyses 328
Iron, colorimetrically..... 250
Iron scale 230
Iron manufacture..... 329
Iron, silicon in..... 219
Iron, volumetric determination, 230, 351
Iron wire 209
Iron ores..... 350
Iron mortar..... 22

Jars, measuring..... 117
Jars, precipitating 86

Keisers apparatus..... 143
Kellogg lamp..... 59
Kjeldahls method..... 306
Koettstorfers number 240, 459
Knapps solution..... 433
Knife-edge.....29, 34

Lactobutyrometer 480
Lakes 531
Lard..... 240
Lead carbonate..... .....209, 215
Lead, refined 174
Lead, determination..... 238
Leather 426
Lemon juice..... 223
Levigation 23

Limits of error..... 555
Lime, determination..... 252
Liquids, sampling 20
Litmus 122
Limits of inaccuracy..... 556
Lixiviation..... 75
Loewenthals method 422
Lovibonds tintometer 261
Lunges burette..... 149
Lux gas-balance 145
Lunges carbon apparatus..... 149

Magnesia, determination..... 252
Malt..... 444
Malt analyses..... 445
Manganese determination.... ... 243
Manganese in iron..... 338
Manganese in ore..... 355
Manganese ores.....322, 350
Manometer..... 299
Mechanical stirrer..... 49
Measuring flasks..... 117
Measuring jars..... 117
Mercury trough..... 140
Methods, attributive 155
Methods, notes on..... 521
Mebus method..... 186
Metals, gases in..... 151
Metals and acids..... 289
Melting point..... 163
Methyl orange..... 122
Methyl alcohol..... 396
Metol..... 233
Meyers funnel..... 62
Milk 476
Minerals, pulverizing..... 21
Moist combustion... 300
Moisture determination 360
Mortars 22, 23
Moores apparatus..... 145
Muffle.....102, 271
Muffle furnace..... 271
Muellers apparatus..... 152

Nickel-copper alloy..... 247
Nitrates in water..... 377
Nitrates in fertilizers..... 388
Nitrites in water..... 379
Nitrogen determination..... 304
Nitrogen in air..... 244
Nitrogen in iron..... 152
Nitrogen in fertilizers..... 388
Nitrogen in water..... 377
Nitric acid, reagent..... 209
Nitroglycerin, glycerol..... 408
Nitrometer..... 144
Normal solutions.....125, 180
Normal solutions, table..... 126
Notes on methods..... 521

Occlusion of impurities..... 531
Official methods..... 558
Oils, mixed, analysis..... 459
Opium analysis 420
Ores, sampling..... 18
Ores, powdering..... 22
Ores, iron and manganese..... 350
Organic analysis, ultimate..... 295
Organic analysis, proximate..... 311
Orsats apparatus 148
Oven, water 27
Oxygen in water..... 374

Pan-supports, balance..... 32
Paper, filter..... 89
Paper pulp..... 89
Parting 273
Penetrability 169
Permanganate, analysis..... 242
Permanganate, reagent..... 210
Permanganate, standard..... 229
Permanganate, oxidation.....188, 301
Percolation..... 51
Phenol 13
Phenylhydrazin..... 434
Phenol-phthalein 122, 209
Phosphorus, determination..... 309
Phosphorus in iron..... 337
Phosphoric acid in ores..... 356
Phosphoric acid, fertilizer..... 382
Pipettes 115
Pipettes, assay..... 115
Pipettes, empirical..... 116
Platinic chloride..... 208
Platinum dishes..... 60
Platinum crucibles 100
Polarization..... 165
Polarimeter 165
Porcelain mortar..... 23
Porcelain crucibles..... 101
Potash in fertilizers..... 386
Potassium chlorate..... 229
Potassium salts, reagents.....209, 210
Potassium permanganate, anal... 242
Potassium hydrate, standard. ... 222
Potassium and sodium, separation 391

Precipitation..... 68
Precipitates, drying..... 103
Precipitates, igniting..... 102
Precipitates, change on ignition .. 106
Precipitates, volume of..... 88
Precipitates, impurities in..... 108
Precipitates, filtering..... 95
Preparation of sample..... 24
Pressure flask..... 50
Proteids of milk..... 484
Proximate organic analysis..... 311
Pulverizing solids..... 21
Pump, vacuum..... 98
Purifying compounds..... 24
Pyrogallol, reagent..... 210

Quantitative analysis..... 561
Quartation..... 273

Radial burner..... 59
Raw sugar, analysis..... 438
Reagents..... 205
Reagents, solutions..... 206
Reagents, calculation..... 183
Receiver..... 64
Reductor..... 341
Residual titration..... 130
Resin acids..... 473
Reichenburgs apparatus..... 150
Refractive index..... 167
Reversal, weighing by..... 38
Rider..... 40
Rider arm..... 32
Roasting..... 100
Routine of separation.....529, 551

Saccharimeter..... 165
Sampling..... 18
Sampling machines..... 21
Sampling shovel..... 18
Sachses solution..... 433
Sanitary analysis..... 568
Sand filter..... 92
Saponification..... 321
Saponification equivalent.... 240, 458
Sand-bath..... 57
Scheiblers apparatus..... 149
Schultze-Tiemanns method..... 389
Scale, iron..... 230
Scorification..... 270
Sealed tubes, heating in..... 50
Segregation..... 19
Separation..... 74
Separation of organic bodies..... 318
Separation of sugars..... 435
Separation, partial..... 85
Separation, mechanical..... 74
Separation by distillation..... 81
Separation by heat..... 80
Separation by electrolysis..... 286
Separation by extraction..... 77
Separation by precipitation..... 82
Separation by solution..... 74
Separatory funnel..... 78
Siegurt and Duerrs apparatus.... 146
Sifting..... 23
Silicon in iron..... 332
Silicon, determination..... 219
Silica in ores..... 354
Silica in silicates..... 251
Silicates..... 251
Silver nitrate, reagent..... 210
Silver assay..... 273
Soaps..... 469
Sodium salts, reagents..... 210
Sodium thiosulfate..... 234
Sodium chloride..... 216
Solution..... 46
Solutions, normal..... 125
Solutions, standard..... 123
Solvents..... 47
Soxhlets apparatus..... 53
Specifications..... 577
Special balances..... 32
Specific gravity of gases..... 162
Specific gravity..... 157
Specific gravity, formulae..... 185
Sprengels tube..... 158
Spot indications..... 119
Spectrum analysis..... 166
Stand, weighing..... 38
Standardizing solutions..... 123
Standard acid..... 221
Standard alkali..... 222
Standard solutions..... 122
Standard permanganate..... 229
Standard methods..... 558
Starch..... 440
Starch sugar, analysis..... 439
Steel works analysis..... 570
Steel, manganese in..... 235
Steel manufacture..... 328
Steel mortar..... 21
Stirring machine..... 48
Still..... 212
Substitution, weighing by..... 38

Sublimation 67
Subnormal solutions 126
Sugars 427
Sugar in urine 503
Sugar of milk 485
Sulfides, roasting 107
Sulfur in coal 361
Sulfur in iron 341
Sulfur in ores 356
Sulfur, determination 277, 308
Sulfuric acid, determination 233
Sulfuric acid, standard 221
Sulfuric acid, reagent 211
Sulfurous acid, reagent 211
Superphosphates, analysis 390

Tables 592
Table, normal solutions 126
Table, indicators 121
Tanning extracts 425
Tannins 421
Terminology 8
Testing the balance 41
Testing the weights 43
Testing volumetric ware 136
Tension aqueous vapor 183, 594
Thoerners tube 56
Tintometer 261
Titration 134
Titration, fractional 132
Thermostat 27
Titanic acid 357
Tobacco, analysis 419
Ton, assay 41
Torsion balance 33
Triangles 102
Turpentine 465
Tube, pressure 50

Ultimate analysis, coal 364
Ultimate organic analysis 295
Units of electricity 281
Urea 498
Urine, composition of 493
Uric acid 497

Vacuum pump 93
Vapor temperature 169
Vegetable matter, burning 105
Vegetable matter, analysis 450
Vibration, weighing by 38
Vinegar 223
Viscosity 168
Viscosimeter 168
Voltaic energy 170
Volumetric analysis 110
Volumetric apparatus 110
Volumetric methods 533
Volumetric solutions 127
Volumetric solutions, normal 125
Volumetric solutions, standard 123
Volumetric analysis, reactions 110
Volumenometer 160

Wash-bottle 97
Washing precipitates 96
Washings, testing 99
Water, natural 366
Water bath 59
Water, distilled 211
Water, weight of 593
Water oven 27
Water-level 27
Weighed filters 100
Weight of water 593
Weight of gases 593
Weight of material for analysis 45
Weighing bottle 46
Weighing, operation of 37
Weighing by reversal 38
Weighing by substitution 38
Weighing by vibrations 38
Weighing in vacuo 39
Weighing, temperature in 38
Weights, atomic, table of 592
Weights, accuracy 41
Weights, assay 41
Weldons mud 324
Westphal balance 159
Wine, analysis 401
Will-Varrentrapp method 305
Wollastonite 251
Wood fiber analysis 450

Xanthin bases 505

Zeisels method 316
Zinc, reagent 212
Zinc, decomposing sulfides 75

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